

Excel with TM

SYSTEMATIC NUMERICAL CHEMISTRY



ORGANIC AND INORGANIC THEORY

FOR XI & XII

IIT-JEE, AIEEE, AIPMT

And Other Competitive Examinations

S. K. Kundra
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The Mole and Chemical-Formulae

- 1. The atomic mass.** The relative atomic mass of an element indicates 'how much' heavier is an atom of the element as compared to one-twelfth of the mass of a carbon-12 atom ($^{12}_6\text{C}$).

$$\text{Relative atomic mass of an element} = \frac{\text{Mass of 1 atom of the element}}{\frac{1}{12} \times \text{Mass of 1 atom of carbon-12}}$$

- 2. Mole.** A collection of 6.023×10^{23} particles is called a mole.
- 3. Avogadro number (N_{Avog}).** The number of particles in a mole is called Avogadro number. It is equal to 6.023×10^{23} .
- 4. Gram-atom or Gram atomic mass.** A gram-atom of an element contains 6.023×10^{23} atoms. It is the mass of 1 mole of the atoms of the element and is equal to the mass in grams that numerically equals its atomic mass in atomic mass units.

Example 1. The relative atomic mass of hydrogen is 1 amu. One gram-atom (mole) of hydrogen weighs 1 gram and contains 6.023×10^{23} hydrogen atoms.

Example 2. The relative atomic mass of sodium is 23 amu. One gram-atom (mole) of sodium weighs 23 grams and contains 6.023×10^{23} sodium atoms.

- 5. Molecular mass.** The relative molecular mass of a compound indicates 'how much' heavier is a molecule of the compound as compared to one-twelfth of the mass of the carbon-12 atom ($^{12}_6\text{C}$).

$$\text{Relative molecular mass of a compound} = \frac{\text{Mass of 1 molecule of the compound}}{\frac{1}{12} \times \text{Mass of 1 atom of carbon-12}}$$

- 6. Gram-mole or Gram molecular mass.** A gram-mole of a compound contains 6.023×10^{23} molecules. It is the mass of 1 mole of the molecules of the compound and is equal to mass in grams that numerically equals its molecular mass in atomic mass units. We say that the relative molecular mass of a compound expressed in grams is equal to one gram-mole.

Example 1. The relative molecular mass of carbon dioxide is 44 amu. One gram-mole of carbon dioxide weighs 44 grams and contains 6.023×10^{23} CO_2 molecules.

Example 2. The relative molecular mass of sodium chloride is 58.5 amu. One gram-mole of sodium chloride weighs 58.5 grams and contains 6.023×10^{23} NaCl units. For ionic-compounds, the term : *formula-mass* instead of molecular mass is used because they consist of aggregates of cations and anions and so do not contain molecules.

7. Calculation of the molecular mass of a compound. The molecular mass of a compound is calculated by adding the relative atomic masses in atomic mass units of all the atoms present in a single molecule.

Example 1. Molecular mass of carbon dioxide. The atomic masses of carbon and oxygen are 12 and 16 amu respectively.

$$\text{Molecular mass of CO}_2 = 1 \times 12 + 2 \times 16 = 44 \text{ amu.}$$

Example 2. Molecular mass of cupric sulphide. The atomic masses of copper and sulphur are 63.5 and 32 amu respectively.

$$\text{Molecular mass of CuS} = 1 \times 63.5 + 1 \times 32 = 95.5 \text{ amu}$$

Example 3. Molecular mass of sulphuric acid. The atomic masses of hydrogen, sulphur and oxygen are 1, 32 and 16 amu respectively.

$$\text{Molecular mass of H}_2\text{SO}_4 = 2 \times 1 + 1 \times 32 + 4 \times 16 = 98 \text{ amu}$$

8. Calculating number of moles

(a) For an assembly of things :

$$\text{Number of moles} = \frac{\text{Number of things}}{6.023 \times 10^{23}}$$

(b) For elements :

$$\begin{aligned} \text{Number of moles} &= \frac{\text{Number of atoms of the element}}{6.023 \times 10^{23}} \\ &= \frac{\text{Mass of the element in grams}}{\text{Gram atomic mass}} \end{aligned}$$

(c) For compounds :

$$\begin{aligned} \text{Number of moles} &= \frac{\text{Number of molecules of the compound}}{6.023 \times 10^{23}} \\ &= \frac{\text{Mass of the compound in grams}}{\text{Gram molecular mass}} \end{aligned}$$

✓ SOLVED PROBLEMS

Problem 1. How many atoms of fluorine are there in 1.9×10^{-6} gram of fluorine? The atomic mass of fluorine is 19 amu.

Solution. 1 mole of fluorine weighs 19 grams and contains 6.023×10^{23} fluorine atoms.

\therefore Number of atoms of fluorine in 1.9×10^{-6} g of fluorine

$$= \frac{6.023 \times 10^{23} \text{ atoms}}{19 \text{ g}} \times 1.9 \times 10^{-6} \text{ g} = 6.023 \times 10^{16} \text{ atoms.}$$

Problem 2. A sample of nitrogen contains 2.8×10^{19} atoms of nitrogen. What is the mass of this collection of atoms? The atomic-mass of nitrogen is 14 amu.

Solution. 1 mole of nitrogen weighs 14 grams and contains 6.023×10^{23} atoms of nitrogen.

$$\begin{aligned} \therefore \text{Mass of } 2.8 \times 10^{19} \text{ atoms of nitrogen} &= \frac{14 \text{ g}}{6.023 \times 10^{23} \text{ atoms}} \times 2.8 \times 10^{19} \text{ atoms} \\ &= 6.5084 \times 10^{-4} \text{ g.} \end{aligned}$$

Problem 3. What is the mass, in grams, of 0.25 mol copper? Cu = 63.5 amu.

Solution. 1 mole of copper weighs 63.5 g.

$$\therefore \text{Mass of 0.25 mol copper} = \left(\frac{63.5 \text{ g}}{\text{mol}} \right) \times 0.25 \text{ mol} = 15.875 \text{ g.}$$

Problem 4. How many atoms of iron are there in 0.75 mol iron? amu of Fe = 55.8.

Solution. 1 mole of iron weighs 55.8 g and contains 6.023×10^{23} iron atoms.

$$\begin{aligned} \therefore \text{Number of atoms in 0.75 mol Fe} &= 6.023 \times 10^{23} \frac{\text{atoms}}{\text{mol}} \times 0.75 \text{ mol} \\ &= 4.52 \times 10^{23} \text{ atoms.} \end{aligned}$$

Problem 5. How many moles of gold are there in 49.25 g gold rod? amu of gold = 197.

Solution. 1 mole of gold weighs 197 g.

$$\therefore \text{Number of moles in 49.25 g gold rod} = \frac{1}{197 \text{ g/mol}} \times 49.25 \text{ g} = 0.25 \text{ mol.}$$

Problem 6. What is the mass of one individual sulphur atom? amu of S = 32.

Solution. 1 mole of sulphur weighs 32 grams and contains 6.023×10^{23} sulphur atoms.

$$\therefore \text{Mass of one S-atom} = \frac{32 \text{ g}}{6.023 \times 10^{23} \text{ atoms}} \times 1 \text{ atom} = 5.313 \times 10^{-23} \text{ g.}$$

Problem 7. How many moles of atoms are there in one atom?

Solution. 1 mole contains 6.023×10^{23} atoms

$$\begin{aligned} \therefore \text{Number of moles in one atom} &= \frac{1 \text{ mol}}{6.023 \times 10^{23} \text{ atoms}} \times 1 \text{ atom} \\ &= 1.66 \times 10^{-24} \text{ mol} \end{aligned}$$

Problem 8. 16.26 milligram of a sample of an element X contains 1.66×10^{20} atoms. What is the atomic mass of the element, X?

Solution. 1 mole of an element contains 6.023×10^{23} atoms.

$$\therefore \text{Mass of } 6.023 \times 10^{23} \text{ atoms} = \frac{16.26 \times 10^{-3} \text{ g}}{1.66 \times 10^{20} \text{ atoms}} \times 6.023 \times 10^{23} \text{ atoms} = 59 \text{ g}$$

\therefore The atomic mass of element 'X' is 59 amu.

Problem 9. The isotopic distribution of potassium is 93.2% ^{39}K and 6.8% ^{41}K . How many ^{41}K atoms are there in 1 gram-atom?

Solution. 1 gram-atom contains 6.023×10^{23} atoms.

$$\begin{aligned} \therefore \text{Number of } ^{41}\text{K atoms in 1 gram-atom} &= \frac{6.8}{100} \times 6.023 \times 10^{23} \text{ atoms} \\ &= 4.1 \times 10^{22} \text{ atoms.} \end{aligned}$$

Problem 10. In making silver ornaments, a certain amount of copper is added to silver to obtain the desired properties. A silver ornament contains 1.0×10^{16} copper atoms per cubic centimetre. What relative masses of silver and copper were mixed to make the ornament? Density of pure silver is 10.5 g cm^{-3} .

Solution. Let us make 1 cm^3 of the product and assume that mixing of copper and silver does not change density of silver.

Number of copper atoms per cubic centimetre = 1.0×10^{10} atoms

1 mole of copper contains 6.023×10^{23} atoms and weighs 63.5 g

$$\text{Mass of Cu to be added} = \frac{63.5 \text{ g}}{6.023 \times 10^{23} \text{ atom}} \times 1.0 \times 10^{10} \text{ atoms} = 1.0543 \times 10^{-12} \text{ g}$$

\therefore 1 cm³ of the ornament contains 1.0543×10^{-12} g copper and 10.5 g silver.

Problem 11. The mass of an atom X is 3.155×10^{-22} g. What is the atomic mass of the element X on the atomic mass unit?

Solution. 1 mole (1 gram-atom) of an element contains 6.023×10^{23} atoms and weighs equal to its atomic mass unit in grams.

$$\therefore 1 \text{ gram-atom} = \frac{(3.155 \times 10^{-22} \text{ g})(6.023 \times 10^{23} \text{ atom})}{1 \text{ atom}} = 190 \text{ g}$$

\therefore The atomic mass of the element X is 190 amu.

Problem 12. A coating of cobalt that is 0.005 cm thick is deposited on a plate that is 0.5 m² in total area. How many atoms of cobalt were deposited on the plate? Density of cobalt = 8.9 g cm⁻³, Co = 59 amu.

Solution.

$$\text{Area of the plate} = 0.5 \text{ m}^2 = 0.5 \times 10^4 \text{ cm}^2$$

$$\text{Thickness of the coating} = 0.005 \text{ cm}$$

$$\text{Volume of cobalt deposited} = 0.005 \text{ cm} \times 0.5 \times 10^4 \text{ cm}^2 = 25 \text{ cm}^3$$

$$\text{Mass of cobalt deposited} = \text{volume} \times \text{density}$$

$$= 25 \text{ cm}^3 \times 8.9 \text{ g cm}^{-3} = 222.5 \text{ g}$$

59 g cobalt contains 6.023×10^{23} cobalt atoms.

$$\begin{aligned} \therefore \text{Number of the Co-atoms in 222.5 g cobalt} &= \frac{6.023 \times 10^{23} \text{ atoms}}{59 \text{ g}} \times 222.5 \text{ g} \\ &= 2.2713 \times 10^{24} \text{ atoms.} \end{aligned}$$

Problem 13. An alloy of metals A and B weighs 36 g and contains atoms A and B in the ratio 2 : 5. The percentage by mass of metal A in the sample is 22.22%. If the atomic mass of A is 40, what is the atomic mass of metal B ?

$$\text{Solution.} \quad \text{Mass of } A \text{ in the alloy} = \frac{22.22 \text{ g}}{100 \text{ g}} \times 36 \text{ g} = 8.0 \text{ g}$$

$$\therefore \quad \text{Mass of metal } B \text{ in the alloy} = 36.0 - 8.0 = 28.0 \text{ g}$$

$$\text{Number of atoms of } A \text{ in the sample} = \frac{6.023 \times 10^{23} \text{ atoms}}{40.0 \text{ g}} \times 8.0 \text{ g}$$

As the ratio of atoms A and B is 2 : 5,

$$\therefore \quad \text{Number of atoms of } B \text{ in the alloy} = \frac{6.023 \times 10^{23} \times 8.0}{40.0} \times \frac{5}{2} \text{ atoms}$$

Since the mass of metal B is 28 g,

$$\begin{aligned} \text{Mass of 1 mole of atoms of } B &= \frac{28 \text{ g} \times 40 \times 2}{6.023 \times 10^{23} \times 8.0 \times 5} \times 6.023 \times 10^{23} \\ &= \frac{28 \times 40 \times 2}{8.0 \times 5} = 56 \text{ g} \end{aligned}$$

\therefore The atomic mass of B is 56 amu.

Problem 14. The density of liquid gallium metal is 6.1 g/cm^3 . What is the volume occupied by 25 gallium atoms? ($\text{Ga} = 69.72 \text{ amu}$)

Solution. 1 mole of gallium (6.023×10^{23}) atoms weighs 69.72 g .

$$\therefore \text{Mass of 25 gallium atoms} = \frac{69.72 \text{ g} \times 25 \text{ atoms}}{6.023 \times 10^{23} \text{ atoms}}$$

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

$$\begin{aligned} \therefore \text{Volume of 25 gallium atoms} &= \frac{69.72 \times 25 \text{ g}}{6.023 \times 10^{23} \times 6.1 \text{ g/cm}^3} \\ &= 4.744 \times 10^{-22} \text{ cm}^3. \end{aligned}$$

Problem 15. What is the mass in grams of one mole of sulphur trioxide? $\text{O} = 16$; $\text{S} = 32 \text{ amu}$.

Solution. Molecular mass of $\text{SO}_3 = 1 \times 32 + 3 \times 16 = 80 \text{ amu}$

1 mole of a compound contains 6.023×10^{23} molecules and weighs equal to molecular mass in grams.

\therefore Mass of 1 mole of $\text{SO}_3 = 80.0 \text{ g}$.

Problem 16. How many molecules are there in 1.625 gram ferric chloride? $\text{Fe} = 56$; $\text{Cl} = 35.5 \text{ amu}$.

Solution. Molecular mass of $\text{FeCl}_3 = 1 \times 56 + 3 \times 35.5 = 162.5 \text{ amu}$

162.5 g FeCl_3 contains 6.023×10^{23} FeCl_3 molecules.

$$\begin{aligned} \therefore \text{Number of molecules in } 1.625 \text{ g FeCl}_3 &= \frac{6.023 \times 10^{23} \text{ molecules}}{162.5 \text{ g}} \times 1.625 \text{ g} \\ &= 6.023 \times 10^{21} \text{ molecules.} \end{aligned}$$

Problem 17. How many oxygen atoms are there in $6.025 \text{ g Ba}_3(\text{PO}_4)_2$? $\text{Ba} = 137.5$; $\text{P} = 31$; $\text{O} = 16 \text{ amu}$.

Solution. Molecular mass of $\text{Ba}_3(\text{PO}_4)_2 = 3 \times 137.5 + 2[31 + 4 \times 16]$
 $= 602.5 \text{ amu}$

$602.5 \text{ g Ba}_3(\text{PO}_4)_2$ contains 6.023×10^{23} molecules.

$$\begin{aligned} \therefore \text{Number of molecules in } 6.025 \text{ g Ba}_3(\text{PO}_4)_2 &= \frac{6.023 \times 10^{23} \text{ molecules}}{602.5 \text{ g}} \times 6.025 \text{ g} \\ &= 6.023 \times 10^{21} \text{ molecules.} \end{aligned}$$

Since 1 molecule of $\text{Ba}_3(\text{PO}_4)_2$ contains 8 oxygen atoms,

$$\begin{aligned} \text{Number of oxygen atoms in } 6.025 \text{ g Ba}_3(\text{PO}_4)_2 &= 8 \times 6.023 \times 10^{21} \\ &= 4.8184 \times 10^{22} \text{ oxygen atoms.} \end{aligned}$$

Problem 18. A sample of sodium hydroxide contains 2.5×10^{10} molecules. What is the mass of this sample? $\text{Na} = 23$; $\text{H} = 1$; $\text{O} = 16 \text{ amu}$.

Solution. Molecular mass of $\text{NaOH} = 1 \times 23 + 1 \times 16 + 1 \times 1 = 40 \text{ amu}$

1 mole of NaOH weighs 40 grams and contains 6.023×10^{23} NaOH molecules.

$$\begin{aligned}\therefore \text{Mass of } 2.5 \times 10^{10} \text{ molecules of NaOH} &= \frac{40 \text{ g} \times 2.5 \times 10^{10} \text{ molecules}}{6.023 \times 10^{23} \text{ molecules}} \\ &= 1.66 \times 10^{-12} \text{ g.}\end{aligned}$$

Problem 19. What is the mass in grams of 0.15 mol of nitrogen dioxide? N = 14; O = 16 amu.

Solution. Molecular mass of NO_2 = $1 \times 14 + 2 \times 16 = 46$ amu
1 mole of NO_2 weighs 46 g and contains 6.023×10^{23} NO_2 molecules.

$$\therefore \text{Mass of 0.15 mol } \text{NO}_2 = \frac{46 \text{ g}}{1 \text{ mol}} \times 0.15 \text{ mol} = 6.9 \text{ g.}$$

Problem 20. What is the mass of one ammonia molecule? N = 14; H = 1 amu.

Solution. Molecular mass of NH_3 = $1 \times 14 + 3 \times 1 = 17$ amu
1 mole of NH_3 weighs 17 grams and contains 6.023×10^{23} NH_3 molecules.

$$\begin{aligned}\therefore \text{Mass of 1 } \text{NH}_3 \text{ molecule} &= \frac{17 \text{ g} \times 1 \text{ molecule}}{6.023 \times 10^{23} \text{ molecules}} \\ &= 2.8225 \times 10^{-23} \text{ g.}\end{aligned}$$

Problem 21. How many moles of O are present in 4.9 grams of H_3PO_4 ? P = 31; O = 16; H = 1 amu.

Solution. Molecular mass of H_3PO_4 = $3 \times 1 + 1 \times 31 + 4 \times 16 = 98$ amu.

$$\begin{aligned}\text{Moles } \text{H}_3\text{PO}_4 \text{ in 4.9 g} &= \frac{\text{Mass of } \text{H}_3\text{PO}_4 \text{ in g}}{\text{Molecular mass}} \\ &= \frac{4.9}{98} = 0.05 \text{ mol}\end{aligned}$$

Since 1 mole of H_3PO_4 contains 4 moles of oxygen

$$\therefore \text{Moles of O} = 4 \times 0.05 \text{ mol} = 0.2 \text{ mol.}$$

Problem 22. How many molecules of benzene (C_6H_6) are there in 1 litre of benzene? Specific gravity of benzene 0.88.

Solution. Mass of 1 litre of benzene = volume \times density
= $1000 \text{ cm}^3 \times 0.88 \text{ g/cm}^3 = 880 \text{ g}$

Molecular mass of benzene, C_6H_6 = $6 \times 12 + 6 \times 1 = 78$ amu

78 g of benzene contains 6.023×10^{23} benzene molecules.

$$\begin{aligned}\therefore \text{Number of benzene molecules in 880 g benzene} &= \frac{6.023 \times 10^{23} \text{ molecule}}{78 \text{ g}} \times 880 \text{ g} \\ &= 6.795 \times 10^{24} \text{ molecules.}\end{aligned}$$

Problem 23. What is the molecular mass of a compound, X, if its 3.0115×10^9 molecules weigh 1.0×10^{-12} g?

Solution. Mass of 6.023×10^{23} molecules

$$= \frac{1.0 \times 10^{-12} \text{ g} \times 6.023 \times 10^{23} \text{ molecules}}{3.0115 \times 10^9 \text{ molecules}} = 200 \text{ g.}$$

\therefore The molecular mass of X is 200 amu.

Problem 24. The mass of one molecule of compound A is 1.984×10^{-22} g. What is the molecular mass of the compound A in atomic mass unit?

Solution. 1 mole of a compound contains 6.023×10^{23} molecules and weighs equal to its molecular mass in grams.

$$\begin{aligned} 1 \text{ gram-mole} &= \frac{1.984 \times 10^{-22} \text{ g}}{1 \text{ molecule}} \times 6.023 \times 10^{23} \text{ molecules/mol} \\ &= 119.5 \text{ g mol}^{-1} \end{aligned}$$

\therefore The molecular mass of compound A is 119.5 amu.

Problem 25. A sample of phosphorus has 0.25 moles of P_4 molecules.

- (i) How many P_4 molecules are there ?
- (ii) How many P atoms are there ?
- (iii) How many moles of P atoms are there in the sample ?
- (iv) What is the mass of the sample ?

Solution. (i) 1 mole of P_4 contains 6.023×10^{23} P_4 molecules

$$\begin{aligned} \therefore \text{Number of } P_4 \text{ molecules in 0.25 mol} &= \frac{6.023 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \times 0.25 \text{ mol} \\ &= 1.506 \times 10^{23} P_4 \text{ molecules.} \end{aligned}$$

(ii) Since 1 P_4 molecule contains 4 P atoms,

$$\begin{aligned} \text{Number of P atoms} &= 4 \times 1.506 \times 10^{23} \\ &= 6.023 \times 10^{23} \text{ P atoms.} \end{aligned}$$

$$(iii) \quad \text{Moles of P atoms} = \frac{1 \text{ mol} \times 6.023 \times 10^{23} \text{ atoms}}{6.023 \times 10^{23} \text{ atom}} = 1 \text{ mol.}$$

$$(iv) \quad \text{Molecular mass of } P_4 = 4 \times 31 = 124 \text{ amu}$$

1 mole of P_4 molecules weighs 124 grams,

$$\therefore \text{Mass of 0.25 mol } P_4 \text{ molecules} = \frac{124 \text{ g}}{1 \text{ mol}} \times 0.25 \text{ mol} = 31.0 \text{ g.}$$

Problem 26. The volume of a drop of water is 0.04 mL. How many H_2O molecules are there in a drop of water ? Density of water = 1.0 g/mL.

$$\begin{aligned} \text{Solution.} \quad \text{Mass of 1 drop of water} &= \text{volume} \times \text{density} \\ &= 0.04 \text{ mL} \times 1.0 \text{ g/mL} = 0.04 \text{ g} \end{aligned}$$

$$\text{Molecular mass of } H_2O = 2 \times 1 + 16 = 18 \text{ amu}$$

18 g H_2O contains 6.023×10^{23} H_2O molecules

$$\begin{aligned} \therefore \text{Number of } H_2O \text{ molecules in 0.04 g } H_2O &= \frac{6.023 \times 10^{23} \text{ molecules}}{18 \text{ g}} \times 0.04 \text{ g} \\ &= 1.3384 \times 10^{21} \text{ molecules.} \end{aligned}$$

Problem 27. How many grams of $Cu(NO_3)_2$ would you need to take to get 1.00 g of copper? $Cu = 63.5$; $N = 14$; $O = 16$ amu.

$$\begin{aligned} \text{Solution.} \quad \text{Molecular mass of } Cu(NO_3)_2 &= 63.5 + 2[14 + 3 \times 16] \\ &= 187.5 \text{ amu} \end{aligned}$$

1 molecule of $\text{Cu}(\text{NO}_3)_2$ contains 1 copper atom

\therefore 187.5 g $\text{Cu}(\text{NO}_3)_2$ contains 63.5 g copper

$$\text{Mass of } \text{Cu}(\text{NO}_3)_2 \text{ needed to take 1 g Cu} = \frac{187.5 \text{ g}}{63.5 \text{ g}} \times 1.0 \text{ g} = 2.9528 \text{ g.}$$

Problem 28. What is the volume occupied by one carbon tetrachloride molecule at 20°C ? The density of carbon tetrachloride is 1.6 g cm^{-3} at 20°C .

Solution. Molecular mass of $\text{CCl}_4 = 1 \times 12 + 4 \times 35.5 = 154 \text{ amu}$

1 mole of CCl_4 (6.023×10^{23} molecules) weighs 154 g

$$\text{Mass of 1 } \text{CCl}_4 \text{ molecule} = \frac{154 \text{ g} \times 1 \text{ molecule}}{6.023 \times 10^{23} \text{ molecules}}$$

$$\begin{aligned} \text{Volume of 1 } \text{CCl}_4 \text{ molecule} &= \frac{\text{Mass}}{\text{Density}} = \frac{154 \text{ g}}{6.023 \times 10^{23} \times 1.6 \text{ g cm}^{-3}} \\ &= 1.598 \times 10^{-22} \text{ cm}^3. \end{aligned}$$

Problem 29. How many years would it take to spend Avogadro's number of rupees at the rate of one million (10 lakh) rupees per second?

(ISM Dhanbad 1992; MLNR 1990)

Solution. Rupees spent in 1 year = Rs. $10^6 \times 3,600 \times 24 \times 365$

\therefore Years required to spend 6.02×10^{23} rupees

$$\begin{aligned} &= \frac{6.02 \times 10^{23}}{10^6 \times 3,600 \times 24 \times 365} \text{ years} \\ &= 1.9 \times 10^{10} \text{ years.} \end{aligned}$$

Problem 30. Weight of one atom of an element is $6.644 \times 10^{-23} \text{ g}$. Calculate g-atom of element in 40 kg. (IIT 1975)

Solution. Weight of 1 atom of element = $6.644 \times 10^{-23} \text{ g}$

\therefore Weight of 6.023×10^{23} atoms of element = $6.644 \times 10^{-23} \times 6.023 \times 10^{23} = 40 \text{ g}$

\therefore 40 g of element has 1 g-atom

$$\therefore 40 \times 10^3 \text{ g of element} = \frac{40 \times 10^3}{40} = 10^3 \text{ g-atom.}$$

Problem 31. Calculate how many methane molecules and how many hydrogen and carbon atoms are there in 25 g of methane? (ISM Dhanbad 1991; MLNR 1990)

Solution. Mol. Mass of $\text{CH}_4 = 16 \text{ g/mol}$

16 g of methane contains (1 mol) = 6.023×10^{23} molecules of CH_4

$$\begin{aligned} \therefore 25 \text{ g of methane contains} &= \frac{6.023 \times 10^{23} \text{ molecules/mol} \times 25 \text{ g}}{16 \text{ g/mol}} \\ &= 9.41 \times 10^{23} \text{ molecules of } \text{CH}_4. \end{aligned}$$

As each molecule of CH_4 contains 1 atom of carbon and 4 atoms of hydrogen

\therefore Number of C atoms = 9.41×10^{23} atoms

and Number of H atoms = $9.41 \times 10^{23} \times 4 = 3.764 \times 10^{24}$ atoms.

Problem 32. Calculate weight of 1 atom of hydrogen.

(Roorkee 1974)

Solution. \therefore Avogadro number of atoms of H weighs 1 g

$$\therefore 1 \text{ atom of H weighs } \frac{1}{6.023 \times 10^{23}} = 1.66 \times 10^{-24} \text{ g.}$$

Problem 33. Calculate the total number of moles present in 12 g of ozone and 32 g of sulphur dioxide in a gaseous mixture. (Andhra Junior Intermediate 1992)Solution. Total number of moles = Moles of ozone + Moles of SO_2

$$\begin{aligned} &= \frac{12 \text{ g}}{(3 \times 16) \text{ g mol}^{-1}} + \frac{32 \text{ g}}{(32 + 32) \text{ g mol}^{-1}} \\ &= \frac{1}{4} \text{ mol} + \frac{1}{2} \text{ mol} = 0.75 \text{ mol.} \end{aligned}$$

Problem 34. Calculate the number of atoms and volume of 1 g He gas at NTP.

(Roorkee 1978)

Solution. (1 Mole) = 4 g He has 6.023×10^{23} atoms

$$\therefore 1 \text{ g He has } \frac{6.023 \times 10^{23}}{4} \text{ atoms} = 1.506 \times 10^{23} \text{ atoms.}$$

As 1 mole of a gas occupies 22.4 litres at N.T.P.

 \therefore 4 g He has volume of N.T.P. = 22.4 litre

$$\therefore 1 \text{ g He has volume at N.T.P.} = \frac{22.4 \text{ L/mol}}{4 \text{ g/mol}} \times 1 \text{ g} = 5.6 \text{ litre.}$$

Problem 35. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C . Calculate the moles of NO_2 in 100 g mixture. (MLNR 1993, IIT 1979)Solution. Molecular Mass of mixture of NO_2 and N_2O_4 = 2 V.D. = $38.3 \times 2 = 76.6$ Let x g of NO_2 be present in 100 g mixture \therefore mass of N_2O_4 = $100 - x$ g \therefore Moles of NO_2 + Moles of N_2O_4 = Moles of mixture

$$\begin{aligned} \frac{x}{46} + \frac{100 - x}{92} &= \frac{100}{76.6} \\ x &= 20.10 \text{ g} \end{aligned}$$

$$\therefore \text{Moles of } \text{NO}_2 \text{ in mixture} = \frac{20.10}{46} = 0.437$$

Problem 36. A metal M of atomic weight 54.94 has a density of 7.42 g/cm^3 . Calculate the volume occupied and the radius of the atom of this metal assuming it to be sphere. (IIT 1977)

Solution. Mass of 1 atom = $\frac{\text{Atomic weight}}{\text{Avogadro number}}$

$$= \text{Volume of atom} \times \text{density}$$

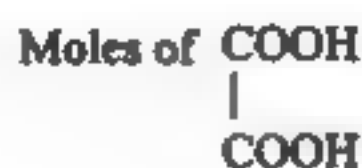
$$\frac{54.94}{6.023 \times 10^{23}} = \frac{4}{3} \pi r^3 \times 7.42$$

$$\therefore r = 1.432 \times 10^{-8} \text{ cm}$$

$$\therefore \text{Volume of CO}_2 \text{ in the gaseous mixture} = \frac{1}{6} \text{ L}$$

$$\text{Volume of CO}_2 \text{ produced when (COOH)}_2 \text{ reacts with H}_2\text{SO}_4 = \frac{1}{6} \text{ L}$$

$$\text{Volume of CO produced when HCOOH reacts with H}_2\text{SO}_4 = 1 - \left(\frac{1}{6} + \frac{1}{6} \right) = \frac{4}{6} \text{ L}$$



Moles of HCOOH

$$\begin{array}{ccc} \frac{1}{6} \text{ L} & : & \frac{4}{6} \text{ L} \\ 1 \text{ mol} & : & 4 \text{ mol} \end{array}$$

(\therefore Volumes are measured at the same T and P).

The oxalic acid and formic acid in the mixture are in the molar ratio of 1 : 4.

Problem 40. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm³/g. If the virus is considered to be a single particle, find its molecular weight. (IIT/JEE 1999)

$$\begin{aligned} \text{Solution. Volume of single virus} &= \pi r^2 l \\ &= \frac{22}{7} \times \left(\frac{150}{2} \times 10^{-8} \right)^2 \times 5000 \times 10^{-8} \text{ cm} \\ &= 0.884 \times 10^{-16} \text{ cm}^3 \end{aligned}$$

$$\text{Weight of single virus} = \frac{0.884 \times 10^{-16} \text{ cm}^3}{0.75 \text{ cm}^3/\text{g}} = 1.178 \times 10^{-16} \text{ g}$$

$$\begin{aligned} \therefore \text{Molecular weight of virus} &= 1.178 \times 10^{-16} \text{ g} \times (6.02 \times 10^{23}) \\ &= 7.09 \times 10^7 \text{ g/mol.} \end{aligned}$$

PROBLEMS FOR PRACTICE

1. How many atoms of chlorine are present in one molecule of CHCl_3 ?
2. How many sulphur atoms are present in six H_2SO_4 molecules ?
3. How many atoms of oxygen are present in $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$?
4. How many atoms of nickel are there in 14.625 g nickel rod ? $\text{Ni} = 58.5$ amu
5. What is the mass of a collection of 2.0×10^{17} bromine atoms ? $\text{Br} = 80$ amu.
6. What is the mass, in grams, of 0.1 mol platinum ? $\text{Pt} = 195$ amu.
7. How many atoms of neon are there in 1.0 gram of neon ? $\text{Ne} = 20$ amu.
8. What is the mass, in grams, of 0.45 mol Ca^{2+} ions ? $\text{Ca} = 40$ amu.
9. How many atoms of zinc are there in 0.016 mol zinc ? $\text{Zn} = 65.5$ amu.
10. How many moles of lead are there in a 2.5 kilogram block of lead ? $\text{Pb} = 207$ amu.
11. What is the mass of one silver atom ? $\text{Ag} = 108$ amu.
12. What is the mass of 2 gram-atoms of nitrogen in an assembly of nitrogen atoms ?
13. How many silver atoms are present in a piece of jewellery weighing 10.78 g?
 $\text{Ag} = 107.8$ amu.
14. 2.49×10^{-18} g sample of an element X contains 2.0×10^4 atoms. What is the atomic mass of element X ?
15. What is the mass of carbon that should be added to 20 kg iron to make a steel containing 0.15% carbon by weight ? What is the ratio of carbon atoms and iron atoms in the steel? $\text{Fe} = 56$; $\text{C} = 12$.
16. A coating of chromium metal that is 0.2 mm thick is deposited on a metal that is 2.5 cm^2 in total area. How many chromium atoms were deposited on the plate ? Density of chromium = 7.2 g/cm^3 . $\text{Cr} = 52$ amu.
17. The density of mercury is 13.6 g/cm^3 . What is the volume occupied by one mercury atom? $\text{Hg} = 100.5$ amu.
18. In a 6 g sample of an alloy of A and B , there are a total of 4.216×10^{22} atoms. The mass of B is twice that of A . If the atomic mass of B is five times that of A , what is the atomic mass of B ?
19. What is the mass of one mole of calcium nitrate, $\text{Ca}(\text{NO}_3)_2$?
 $\text{Ca} = 40$; $\text{N} = 14$; $\text{O} = 16$.
20. What is the mass of 0.04 mol CO_2 ?
21. How many molecules are present in 0.05 mol of carbon monoxide ?
22. How many molecules are present in 1.5 gram of ammonia gas ?
23. How many molecules are there in 0.01 gram of propane, C_3H_8 ?
24. How many chlorine atoms are there in 0.99 gram, carbonyl chloride, COCl_2 ?
 $\text{Cl} = 35.5$ amu.
25. How many aluminium atoms are there in 0.5 g aluminium nitride, AlN ?
 $\text{Al} = 27$ amu.
26. How many moles of O_3 are present in a sample of pure O_3 containing 0.45 mol of O atoms?
27. A sample of ferric iodide contains 3.0115×10^{20} molecules. What is the mass of this sample ? $\text{Fe} = 56$; $\text{I} = 127$ amu.
28. What is the mass in grams of 0.025 mol of thionyl bromide, SOBr_2 ? $\text{S} = 32$, $\text{Br} = 80$.

29. What is the mass of 1 formula unit of nickel fluoride ? $\text{Ni} = 58.5$; $\text{F} = 19$.
30. How many moles of hydrogen are there in 0.925 g $\text{Ca}(\text{OH})_2$? $\text{Ca} = 40$ amu.
31. How many molecules of water are there in 1 litre of water ? The density of water is 1.0 g/ml.
32. Calculate the mass of a water molecule.
33. What is the molecular mass of an alcohol, $\text{R} - \text{OH}$, if its 2.0×10^3 molecules weigh 1.063×10^{-19} g ?
34. The volume of a drop of nitrobenzene is 0.05 cm^3 . How many molecules are there in this drop of nitrobenzene ? The specific gravity of nitrobenzene is 1.203.
35. What is the volume occupied by a molecule of liquid HCN at 22°C ? The density of HCN at 22°C is 0.70 g/cm^3 .
36. How many grams of KClO_3 would you need to take to get 0.5 g of potassium ?
37. Calculate the mass of one molecule of carbon disulphide, CS_2 .
38. Calculate the mass in grams of hydrogen sulphide that contains one-half as many molecules of H_2S as there are atoms in 100 grams of iron (Fe).
39. Which has more molecules, 4 moles of calcium nitrate or 1 kg of PbCl_2 ?
40. A sample of NO_2 gas weighs 10 mg. If 1.8×10^{19} molecules of NO_2 are removed from this sample, how many moles of NO_2 are left ?
41. In rhombic sulphur, sulphur atoms are joined together in a ring of eight producing the molecules S_8 . Determine for a crystal having a volume of 1.05 cm^3 (a) number of moles of S_8 molecules present (b) total number of sulphur atoms. Density of rhombic sulphur = 2.07 g/cm^3 .
42. You are given equal volumes of two different gases A and B at the same temperature and pressure. Mass of A is 1.20 g and that of B is 2.56 g.
 - (a) What is the mass of 1 molecule of A as compared to mass of 1 molecule of B ?
 - (b) If A is oxygen gas, what is the molecular mass of B ?

ANSWERS

- | | | |
|--------------------------------------|--|--|
| 1. 3 | 2. 6 | 3. 13 |
| 4. 1.5058×10^{23} | 5. $2.6565 \times 10^{-5} \text{ g}$ | 6. 19.5 g |
| 7. 3.0115×10^{23} | 8. 18 g | 9. 9.6368×10^{21} |
| 10. 12.1 mol | 11. $1.7931 \times 10^{-22} \text{ g}$ | 12. 28 g |
| 13. 6.023×10^{22} | 14. 75 | 15. 30 g; 1 : 143 |
| 16. 4.169×10^{21} | 17. $2.4477 \times 10^{-23} \text{ cm}^3$ | 18. 200 amu |
| 19. 164 g | 20. 1.76 g | 21. 3.0115×10^{22} |
| 22. 5.314×10^{22} | 23. 1.3688×10^{20} | 24. 1.2046×10^{23} |
| 25. 7.345×10^{21} | 26. 0.15 mol | 27. 0.2185 g |
| 28. 5.2 g | 29. $1.287 \times 10^{-22} \text{ g}$ | 30. 0.025 mol |
| 31. 3.344×10^{25} | 32. $2.99 \times 10^{-23} \text{ g}$ | 33. 32 amu |
| 34. 2.945×10^{20} | 35. $6.4 \times 10^{-23} \text{ cm}^3$ | 36. 1.5705 g |
| 37. $1.26 \times 10^{-22} \text{ g}$ | 38. 30.6 g | 39. 4 moles $\text{Ca}(\text{NO}_3)_2$ |
| 40. $1.9 \times 10^{-4} \text{ mol}$ | 41. (a) 0.0084 mol; (b) 4.0×10^{22} | 42. (a) 2.22, (b) 70.04 |

Percentage Composition of Compounds

- 1. Percent-composition.** The mass of each element present in a compound is expressed in terms of percent by mass. This is known as percentage-composition and is calculated from the formula of the compound. From the atomic masses of the elements and the formula of the compound, we can calculate the number of moles of each element or mass of each element in a mole of the compound.

$$\% \text{ composition} = \frac{\text{Mass of element in sample}}{\text{Total mass of sample}} \times 100$$

- 2. Empirical formula or simplest formula.** The empirical formula of a compound is the simplest whole number ratio of the atoms of elements present in its one molecule. It is written in place of a molecular formula when molecular mass of the substance is indefinite or not known. Sand which consists of large aggregates of oxygen and silicon in the ratio 2 : 1 is represented by the formula SiO_2 instead of Si_xO_{2x} , for sake of simplicity. The ionic-compounds such as sodium chloride are represented by simple formulae as they do not contain molecules.
- 3. Determination of empirical formula.** The empirical formula of a compound is calculated by the following steps :
- Calculate percentage composition of elements in the compound.
 - Divide these percentages by the respective atomic masses of the elements.
 - Divide the numbers obtained by the lowest number. If the numbers obtained are not whole numbers, convert them to the nearest whole number.
- 4. Molecular formula.** (a) The molecular formula of a compound shows the actual ratio of atoms of the elements present in its one molecule. For example, methyl alcohol, CH_4O (CH_3OH), shows that one molecule of methanol contains one carbon atom, four hydrogen atoms and one oxygen atom. In many compounds, the molecular formula is the same as the empirical formula.
- (b) **Determination of molecular formula :**
- Calculate empirical formula mass using empirical formula and atomic masses of the elements.
 - Calculate the ratio of molecular mass and empirical formula mass.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

- (iii) Calculate molecular formulae by multiplying empirical formula by the value n .

$$\text{Molecular formula} = n \times \text{Empirical formula}$$

✓ SOLVED PROBLEMS

Problem 1. What is the percentage of aluminium in Al_2O_3 ? $\text{Al} = 27$; $\text{O} = 16$ amu.

Solution. Molecular mass of $\text{Al}_2\text{O}_3 = 2 \times 27 + 3 \times 16 = 102$ amu

1 mole of Al_2O_3 weighs 102 g

1 mole of Al_2O_3 contains 2 mol of Al

Mass of 2 mol of Al = $2 \times 27 = 54$ g

$$\begin{aligned}\text{Percentage of Al} &= \frac{\text{Mass of Al}}{\text{Mass of sample}} \times 100 \\ &= \frac{54 \text{ g}}{102 \text{ g}} \times 100 = 52.94\%.\end{aligned}$$

Problem 2. Glucose is a physiological sugar. What is mass % C, mass % H and mass % O in glucose, $\text{C}_6\text{H}_{12}\text{O}_6$?

Solution. 1 mole of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, contains 6 mol carbon, 12 mol hydrogen and 6 mol oxygen.

Mass of 6 mol carbon = $6 \times 12 = 72$ g C

Mass of 12 mol hydrogen = $12 \times 1 = 12$ g H

Mass of 6 mol oxygen = $6 \times 16 = 96$ g O

\therefore Mass of 1 mol glucose = $72 + 12 + 96 = 180$ g

$$(a) \quad \text{Mass \% C} = \frac{\text{Mass of carbon}}{\text{Mass of sample}} \times 100 = \frac{72 \text{ g}}{180 \text{ g}} \times 100 = 40\% \text{ C}$$

$$(b) \quad \text{Mass \% H} = \frac{\text{Mass of hydrogen}}{\text{Mass of sample}} \times 100 = \frac{12 \text{ g}}{180 \text{ g}} \times 100 = 6.67\% \text{ H}$$

$$(c) \quad \text{Mass \% O} = \frac{\text{Mass of oxygen}}{\text{Mass of sample}} \times 100 = \frac{96 \text{ g}}{180 \text{ g}} \times 100 = 53.33\% \text{ O}.$$

Problem 3. What is the percentage composition of each element in zinc phosphate, $\text{Zn}_3(\text{PO}_4)_2$? $\text{Zn} = 65.5$; $\text{P} = 31$; $\text{O} = 16$ amu.

Solution. 1 mole of $\text{Zn}_3(\text{PO}_4)_2$ contains 3 mol of zinc, 2 mol of phosphorus and 8 mol of oxygen.

Mass of 3 mol of Zn = $3 \times 65.5 = 196.5$ g

Mass of 2 mol of P = $2 \times 31 = 62$ g

Mass of 8 mol of O = $8 \times 16 = 128$ g

Mass of 1 mol of $\text{Zn}_3(\text{PO}_4)_2 = 196.5 + 62 + 128 = 386.5$ g

$$\begin{aligned}(a) \quad \text{Percentage composition of Zn} &= \frac{\text{Mass of Zn}}{\text{Mass of sample}} \times 100 \\ &= \frac{196.5 \text{ g}}{386.5 \text{ g}} \times 100 = 50.84\% \text{ Zn}\end{aligned}$$

$$\begin{aligned}(b) \quad \text{Percentage composition of P} &= \frac{\text{Mass of P}}{\text{Mass of sample}} \times 100 \\ &= \frac{62 \text{ g}}{386.5 \text{ g}} \times 100 = 16.04\% \text{ P}\end{aligned}$$

$$\begin{aligned}
 (c) \quad \text{Percentage composition of O} &= \frac{\text{Mass of O}}{\text{Mass of sample}} \times 100 \\
 &= \frac{128 \text{ g}}{386.5 \text{ g}} \times 100 = 33.12\% \text{ O}
 \end{aligned}$$

Problem 4. A pure sample of cobalt chloride weighing 1.30 g was found to contain 0.59 g cobalt and 0.71 g chlorine on quantitative analysis. What is the percentage composition of cobalt chloride?

$$\begin{aligned}
 \text{Solution. } \% \text{ Co} &= \frac{\text{Mass of cobalt}}{\text{Mass of sample}} \times 100 = \frac{0.59 \text{ g}}{1.30 \text{ g}} \times 100 = 45.4\% \text{ Co} \\
 \% \text{ Cl} &= \frac{\text{Mass of chlorine}}{\text{Mass of sample}} \times 100 = \frac{0.71 \text{ g}}{1.30 \text{ g}} \times 100 = 54.6\% \text{ Cl.}
 \end{aligned}$$

Problem 5. A pure sample of ethylamine was quantitatively analysed for nitrogen. 0.0275 g of the pure sample was found to contain 0.007 g nitrogen. What is mass % nitrogen in ethylamine?

$$\text{Solution. Mass \% N} = \frac{\text{Mass of N}}{\text{Mass of sample}} \times 100 = \frac{0.007 \text{ g}}{0.0275 \text{ g}} \times 100 = 25.5\% \text{ N.}$$

Problem 6. 0.45 g of an organic compound containing only carbon, hydrogen and nitrogen on combustion gave 1.1 g CO_2 and 0.3 g water. What is % C, % H and % N in the organic compound?

Solution. Mass of organic compound, $w = 0.45 \text{ g}$

Mass of CO_2 , $w_1 = 1.1 \text{ g}$

Mass of water, H_2O , $w_2 = 0.3 \text{ g}$

1 mol C = 1 mol CO_2

12 g = 44 g CO_2

$$\begin{aligned}
 (a) \quad \text{Percentage of carbon} &= \frac{12 \text{ g}}{44 \text{ g}} \times \frac{\text{Mass of } \text{CO}_2}{\text{Mass of sample}} \times 100 \\
 &= \frac{12 \text{ g}}{44 \text{ g}} \times \frac{1.1 \text{ g}}{0.45 \text{ g}} \times 100 = 66.7\% \text{ C}
 \end{aligned}$$

(b) 2 mol H = 1 mol H_2O

2 g H = 18 g H_2O

$$\begin{aligned}
 \text{Percentage of hydrogen} &= \frac{2 \text{ g}}{18 \text{ g}} \times \frac{\text{Mass of } \text{H}_2\text{O}}{\text{Mass of sample}} \times 100 \\
 &= \frac{2 \text{ g}}{18 \text{ g}} \times \frac{0.3 \text{ g}}{0.45 \text{ g}} \times 100 = 7.4\% \text{ H}
 \end{aligned}$$

$$\begin{aligned}
 (c) \quad \% \text{ N} &= 100 - [\% \text{ C} + \% \text{ H}] \\
 &= 100 - [66.7 + 7.4] = 25.9\% \text{ N.}
 \end{aligned}$$

EMPIRICAL FORMULA & MOLECULAR FORMULA

Problem 7. What is the empirical formula of a compound that contains 22% S and 78% F? S = 32, F = 19 amu.

Solution.

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|--------------------------|---------------------------|--------------|
| S | 22 | 32 | $\frac{22}{32} = 0.69$ | $\frac{0.69}{0.69} = 1$ | 1 |
| F | 78 | 19 | $\frac{78}{19} = 4.1$ | $\frac{4.1}{0.69} = 5.94$ | 6 |

∴ The empirical formula of the compound is SF_6 .

Problem 8. A substance used as a water softner has the following mass percent composition : 42.07% sodium, 18.9% phosphorus and 39.04% oxygen. Determine the empirical formula of the compound. Na = 23, P = 31, O = 16.

Solution.

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|---------------------------|--------------------------|--------------|
| Na | 42.07 | 23 | $\frac{42.07}{23} = 1.83$ | $\frac{1.83}{0.61} = 3$ | 3 |
| P | 18.9 | 31 | $\frac{18.9}{31} = 0.61$ | $\frac{0.61}{0.61} = 1$ | 1 |
| O | 39.04 | 16 | $\frac{39.04}{16} = 2.44$ | $\frac{2.44}{0.61} = 4$ | 4 |

∴ The empirical formula of the compound is Na_3PO_4 .

Problem 9. An organic compound contains 43.98% C, 2.09% H and 37.2% Cl. Calculate its empirical formula. C = 12 ; H = 1 ; Cl = 35.5 ; O = 16 amu.

Solution. Percentage of oxygen = $100 - (43.98 + 2.09 + 37.2) = 16.73\%$

Calculation of empirical formula :

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|-----------------------------|----------------------------|--------------|
| C | 43.98 | 12 | $\frac{43.98}{12} = 3.66$ | $\frac{3.66}{1.046} = 3.5$ | 7 |
| H | 2.09 | 1 | $\frac{2.09}{1} = 2.09$ | $\frac{2.09}{1.046} = 2$ | 4 |
| Cl | 37.2 | 35.5 | $\frac{37.2}{35.5} = 1.047$ | $\frac{1.047}{1.046} = 1$ | 2 |
| O | 16.73 | 16 | $\frac{16.73}{16} = 1.046$ | $\frac{1.046}{1.046} = 1$ | 2 |

∴ The empirical formula of the compound is $\text{C}_7\text{H}_4\text{O}_2\text{Cl}_2$.

Problem 10. Calculate the empirical formula of the compound whose percentage composition is C = 21.9%, H = 4.6% and Br = 73.4%. C = 12 ; H = 1 ; Br = 80 amu.

Solution.

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|--------------------------|----------------------------|--------------|
| C | 21.9 | 12 | $\frac{21.9}{12} = 1.83$ | $\frac{1.83}{0.92} = 1.99$ | 2 |
| H | 4.6 | 1 | $\frac{4.6}{1} = 4.6$ | $\frac{4.6}{0.92} = 5$ | 5 |
| Br | 73.4 | 80 | $\frac{73.5}{80} = 0.92$ | $\frac{0.92}{0.92} = 1$ | 1 |

∴ The empirical formula of the compound is C₂H₅Br.

Problem 11. What is the molecular formula of a compound that contains 47.4% S and 52.6% Cl? The molecular mass of the compound as determined experimentally is 135 g mol⁻¹?

Solution.

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|----------------------------|--------------------------|--------------|
| S | 47.4 | 32 | $\frac{47.4}{32} = 1.48$ | $\frac{1.48}{1.48} = 1$ | 1 |
| Cl | 52.6 | 35.5 | $\frac{52.6}{35.5} = 1.48$ | $\frac{1.48}{1.48} = 1$ | 1 |

∴ The empirical formula of the compound is SCl.

Calculation of molecular formula.

$$\text{Empirical formula mass} = 1 \times 32 + 1 \times 35.5 = 67.5 \text{ amu}$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{135}{67.5} = 2$$

$$\begin{aligned} \therefore \text{Molecular formula} &= n \times \text{Empirical formula} \\ &= 2 \times \text{SCl} = \text{S}_2\text{Cl}_2. \end{aligned}$$

Problem 12. The mass percent composition of a substance is 24.7% Ca, 1.24% H, 14.8% C and 59.3% O. Calculate the molecular-formula of the substance if its molecular mass is 162 amu?

Solution.

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|--------------------------|--------------------------|--------------|
| Ca | 24.7 | 40 | $\frac{24.7}{40} = 0.62$ | $\frac{0.62}{0.62} = 1$ | 1 |
| H | 1.24 | 1 | $\frac{1.24}{1} = 1.24$ | $\frac{1.24}{0.62} = 2$ | 2 |

| | | | | | |
|---|------|----|--------------------------|----------------------------|---|
| C | 14.8 | 12 | $\frac{14.8}{12} = 1.23$ | $\frac{1.23}{0.62} = 2$ | 2 |
| O | 59.3 | 16 | $\frac{59.3}{16} = 3.71$ | $\frac{3.71}{0.62} = 5.98$ | 6 |

∴ The empirical formula of the compound is $\text{CaH}_2\text{C}_2\text{O}_6$.

Calculation of molecular formula.

$$\text{Empirical formula mass} = 40 + 2 \times 1 + 2 \times 12 + 6 \times 16 = 162$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{162}{162} = 1$$

∴ Molecular formula = $n \times \text{Empirical formula}$

$$= 1 \times \text{CaH}_2\text{C}_2\text{O}_6$$

$$= \text{CaH}_2\text{C}_2\text{O}_6 \quad \text{or} \quad \text{Ca}(\text{HCO}_3)_2$$

Problem 13. A carbohydrate contains 40.0% C, 6.73% H and 53.3% O and has a molecular weight of 180.2. Calculate its molecular formula.

Solution.

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|--------------------------|----------------------------|--------------|
| C | 40.0 | 12 | $\frac{40.0}{12} = 3.33$ | $\frac{3.33}{3.33} = 1$ | 1 |
| H | 6.73 | 1 | $\frac{6.73}{1} = 6.73$ | $\frac{6.73}{3.33} = 2.02$ | 2 |
| O | 53.3 | 16 | $\frac{53.3}{16} = 3.33$ | $\frac{3.33}{3.33} = 1$ | 1 |

∴ The empirical formula of the compound is CH_2O .

$$\text{Empirical formula mass} = 1 \times 12 + 2 \times 1 + 1 \times 16 = 30$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{180.2}{30} = 6$$

∴ Molecular formula = $n \times \text{Empirical formula}$

$$= 6 \times \text{CH}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6$$

Problem 14. A compound of carbon, hydrogen and nitrogen contains three elements in the respective ratio of 9 : 1 : 3.5. Calculate the empirical formula. If the molecular weight is 108, what is its molecular formula?

Solution.

| Element | Mass ratio | Atomic mass | Atomic ratio | Divided by lowest number | Simple ratio |
|---------|------------|-------------|-----------------------|--------------------------|--------------|
| Carbon | 9 | 12 | $\frac{9}{12} = 0.75$ | $\frac{0.75}{0.25} = 3$ | 3 |

| | | | | | |
|----------|-----|----|-------------------------|-------------------------|---|
| Hydrogen | 1 | 1 | $\frac{1}{1} = 1$ | $\frac{1}{0.25} = 4$ | 4 |
| Nitrogen | 3.5 | 14 | $\frac{3.5}{14} = 0.25$ | $\frac{0.25}{0.25} = 1$ | 1 |

∴ The empirical formula of the compound is C_3H_4N .

$$\text{Empirical formula mass} = 3 \times 12 + 4 \times 1 + 1 \times 14 = 54$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{108}{54} = 2$$

$$\begin{aligned}\therefore \text{Molecular formula} &= n \times \text{Empirical formula} \\ &= 2 \times C_3H_4N = C_6H_8N_2.\end{aligned}$$

Problem 15. A certain compound containing only carbon and oxygen has an approximate molecular weight of 290. On analysis it is found to contain exactly 50% by weight of each element. What is the molecular formula of the compound?

Solution.

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|--------------------------|----------------------------|--------------|
| Carbon | 50 | 12 | $\frac{50}{12} = 4.17$ | $\frac{4.17}{3.13} = 1.33$ | 4 |
| Oxygen | 50 | 16 | $\frac{50}{16} = 3.13$ | $\frac{3.13}{3.13} = 1$ | 3 |

∴ The empirical formula of the compound is C_4O_3 .

$$\text{Empirical formula mass} = 4 \times 12 + 3 \times 16 = 96$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{290}{96} \approx 3$$

$$\therefore \text{Molecular formula} = 3 \times C_4O_3 = C_{12}O_9.$$

Problem 16. A 0.534 g of a sample of haemoglobin on analysis was found to contain 0.34% Fe. If each haemoglobin molecule has four Fe^{2+} ions, what is the molecular mass of haemoglobin?

Solution. 1 mole haemoglobin = 4 moles Fe

$$M \text{ g haemoglobin} = 4 \times 56 = 224 \text{ g Fe}$$

0.34 g Fe is contained in 100 g haemoglobin

$$224 \text{ g Fe is contained in } \frac{100}{0.34} \times 224 = 65882.4 \text{ g}$$

∴ Molecular mass of haemoglobin is $65882.4 \text{ g mol}^{-1}$.

Problem 17. The molecular mass of an iodide of tin is 626.5 amu. What is the empirical formula for this substance? I = 127, Sn = 118.5 amu.

Solution. Let the empirical formula of the substance be SnI_x .

$$\text{Mass of 1 mol Sn} = 118.5 \text{ g}$$

$$\text{Mass of } x \text{ mol I} = x \times 127 \text{ g}$$

$$\text{Mass of 1 mol SnI}_x = 626.5 \text{ g}$$

$$\therefore 118.5 + 127x = 626.5 \text{ g}$$

$$127x = 626.5 - 118.5 = 508$$

$$x = \frac{508}{127} = 4$$

Therefore, molecular formula of the substance is SnI_4 .

This is also the empirical formula because Sn and I have the simple ratio 1 : 4.

Problem 18. A 0.2075 g sample of an oxide of cobalt on analysis was found to contain 0.1475 g cobalt. Calculate the empirical formula of the oxide. Co = 59 amu.

Solution. (a) Mass of Co + Mass of O = Mass of cobalt oxide

$$\text{Mass of O} = \text{Mass of cobalt oxide} - \text{Mass of Co}$$

$$= 0.2075 \text{ g} - 0.1475 \text{ g} = 0.06 \text{ g}$$

$$\begin{aligned} (b) \quad \text{Moles of Co in the oxide} &= \frac{\text{Mass of Co}}{\text{Atomic mass of cobalt}} \\ &= \frac{0.1475 \text{ g}}{59 \text{ g/mol}} = 0.0025 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Moles of O in the oxide} &= \frac{\text{Mass of O}}{\text{Atomic mass of oxygen}} \\ &= \frac{0.06 \text{ g}}{16 \text{ g/mol}} = 0.00375 \text{ mol} \end{aligned}$$

$$(c) \quad \text{Mole ratio } \frac{\text{Co}}{\text{O}} = \frac{0.0025}{0.00375} = 0.67 = \frac{2}{3}$$

(d) Since the mole ratio of atoms in a sample of a compound is equal to the ratio of atoms in its formula, the empirical formula of the oxide of cobalt is Co_2O_3 .

Problem 19. 0.1653 g aluminium reacts completely with 0.652 g chlorine to form a chloride of aluminium.

(a) What is the empirical formula of the compound?

(b) If the approximate molecular mass of the gaseous compound is 267 amu, calculate the molecular formula of the gaseous compound.

$$\begin{aligned} \text{Solution. (a) Moles of Al in the chloride} &= \frac{\text{Mass of Al}}{\text{Atomic mass of Al}} \\ &= \frac{0.1653 \text{ g}}{27 \text{ g/mol}} = 0.0061 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Moles of Cl in the chloride} &= \frac{\text{Mass of Cl}}{\text{Atomic mass of Cl}} \\ &= \frac{0.652 \text{ g}}{35.5 \text{ g/mol}} = 0.0184 \text{ mol} \end{aligned}$$

$$(b) \quad \text{Mole ratio } \frac{\text{Al}}{\text{Cl}} = \frac{0.0061}{0.0184} = \frac{1}{3}$$

(c) Therefore, the empirical formula of the chloride is AlCl_3 .

(d) Empirical formula mass of $\text{AlCl}_3 = 27 + 3 \times 35.5 = 133.5$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{267}{133.5} = 2$$

$$\begin{aligned}\therefore \text{Molecular formula} &= n \times \text{Empirical formula} \\ &= 2 \times \text{AlCl}_3 = \text{Al}_2\text{Cl}_6\end{aligned}$$

Problem 20. A 12.4 g sample of phosphorus reacts with 9.6 g oxygen to form 18.9 g P_4O_6 . If the atomic mass of oxygen is 16.0 amu, calculate the atomic mass of phosphorus.

$$\begin{aligned}\text{Solution. (a) Moles of P} &= \frac{\text{Mass of P}}{\text{Atomic mass of P}} = \frac{12.4 \text{ g}}{x \text{ g/mol}} \\ \text{Moles of O} &= \frac{\text{Mass of O}}{\text{Atomic mass of O}} = \frac{9.6 \text{ g}}{16 \text{ g/mol}} = 0.6 \text{ mol}\end{aligned}$$

$$(b) \quad \text{Mole ratio } \frac{\text{P}}{\text{O}} = \frac{4}{6} = \frac{12.4/x}{0.6}$$

$$\text{or} \quad x = \frac{12.4}{0.6} \times \frac{6}{4} = 31 \text{ g mol}^{-1}.$$

Problem 21. Cysteine is a sulphur containing amino acid. A 0.3025 g sample of pure cysteine contains 0.09 carbon, 0.0175 g hydrogen, 0.08 g oxygen, 0.035 g nitrogen and 0.08 g sulphur. What is the empirical formula of the compound? If the molecular mass of cysteine is 121.16 amu, what is the molecular formula of the compound?

$$\text{Solution. (a) Moles of C} = \frac{\text{Mass of C}}{\text{Atomic mass of C}} = \frac{0.09 \text{ g}}{12 \text{ g/mol}} = 0.0075 \text{ mol C}$$

$$\text{Moles of H} = \frac{\text{Mass of H}}{\text{Atomic mass of H}} = \frac{0.0175 \text{ g}}{1 \text{ g/mol}} = 0.0175 \text{ mol H}$$

$$\text{Moles of O} = \frac{\text{Mass of O}}{\text{Atomic mass of O}} = \frac{0.08 \text{ g}}{16 \text{ g/mol}} = 0.005 \text{ mol O}$$

$$\text{Moles of N} = \frac{\text{Mass of N}}{\text{Atomic mass of N}} = \frac{0.035 \text{ g}}{14 \text{ g/mol}} = 0.0025 \text{ mol N}$$

$$\text{Moles of S} = \frac{\text{Mass of S}}{\text{Atomic mass of S}} = \frac{0.08 \text{ g}}{32 \text{ g/mol}} = 0.0025 \text{ mol S}$$

$$(b) \quad \begin{array}{cccccc} \text{Mole ratio :} & \text{C} & : & \text{H} & : & \text{O} & : & \text{N} & : & \text{S} \\ & 0.0075 & : & 0.0175 & : & 0.005 & : & 0.0025 & : & 0.0025 \\ & 3 & : & 7 & : & 2 & : & 1 & : & 1 \end{array}$$

The empirical formula of cysteine is $\text{C}_3\text{H}_7\text{O}_2\text{NS}$.

$$\text{Empirical formula mass} = 3 \times 12 + 7 \times 1 + 2 \times 16 + 1 \times 14 + 1 \times 32 = 121 \text{ amu}$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{121.16}{121} \approx 1$$

$$\begin{aligned}\therefore \text{Molecular formula} &= n \times \text{Empirical formula} \\ &= 1 \times \text{C}_3\text{H}_7\text{O}_2\text{NS} = \text{C}_3\text{H}_7\text{O}_2\text{NS}.\end{aligned}$$

Problem 22. What is the simplest formula of a compound that consists of 0.25 gram-atom of silicon per 0.50 gram-atom of oxygen?

Solution.
$$\frac{\text{Si}}{\text{O}} = \frac{0.25 \text{ gram atom}}{0.50 \text{ gram atom}} = \frac{1}{2}$$

\therefore The simplest formula of the compound is SiO_2 .

Problem 23. An organic compound consists of 6.023×10^{23} carbon atoms, 1.8069×10^{24} hydrogen atoms and 3.0115×10^{23} oxygen atoms. What is its simplest formula?

Solution.
$$\text{Moles of C} = \frac{6.023 \times 10^{23} \text{ atoms C}}{6.023 \times 10^{23} \text{ atoms/mol}} = 1 \text{ mol C}$$

$$\text{Moles of H} = \frac{1.8069 \times 10^{24} \text{ atoms H}}{6.023 \times 10^{23} \text{ atoms/mol}} = 3 \text{ mol H}$$

$$\text{Moles of O} = \frac{3.0115 \times 10^{23} \text{ atoms}}{6.023 \times 10^{23} \text{ atoms}} = 0.5 \text{ mol}$$

\therefore Simplest ratio $\text{C} : \text{H} : \text{O} :: 1 : 3 : 0.5$
 $:: 2 : 6 : 1$

\therefore The simplest formula is $\text{C}_2\text{H}_6\text{O}$.

Problem 24. 1.5276 g of CdCl_2 was found to contain 0.9367 g of Cd. Calculate atomic weight of Cd. (IIT/JEE 1973)

Solution.
$$\text{Weight of Cd} = 0.9367 \text{ g}$$

\therefore
$$\text{Weight of Cl} = 1.5276 \text{ g} - 0.9367 \text{ g} = 0.5909 \text{ g}$$

For CdCl_2 , Equivalent of Cd = Equivalent of Cl

$$\frac{0.9367}{E} = \frac{0.5909}{35.5}$$

\therefore
$$E = 56.275$$

\therefore
$$\begin{aligned} \text{Atomic weight} &= \text{Eq. wt.} \times \text{Valency} \\ &= 56.275 \times 2 = 112.55 \text{ amu.} \end{aligned}$$

Problem 25. A hydrated sulphate of metal contained 8.1% metal and 43.2% SO_4^{-2} by weight. The specific heat of metal is 0.24 cal/g. What is the formula of hydrated sulphate? (IIT/JEE 1997)

Solution. Let the formula of hydrated sulphate be $\text{M}_x(\text{SO}_4)_y \cdot n\text{H}_2\text{O}$ where n is valence of metal.

$$\text{At. wt.} \times \text{specific heat} = 6.4$$

\therefore
$$\text{At. wt. of metal} = \frac{6.4}{0.24} = 26.67$$

Now
$$\text{Eq. of metal} = \text{Equivalent of } \text{SO}_4^{-2}$$

$$\frac{8.1}{\text{At. wt.}/n} = \frac{43.2}{96/2}$$

\therefore
$$n = \frac{43.2 \times 2 \times \text{At. wt.}}{96 \times 8.1}$$

$$= \frac{43.2 \times 2 \times 26.67}{96 \times 8.1} = 2.96 \approx 3; \quad n \approx 3$$

$$\therefore \text{Exact at. wt. of metal} = 9 \times 3 = 27$$

$$\therefore \text{M. wt of } M_2(SO_4)_3 \cdot mH_2O = 2 \times 27 + 96 \times 3 + 18m = 342 + 18m$$

$$(342 + 18m) \text{ g } M_2(SO_4)_3 \cdot mH_2O \text{ has } 18m \text{ g } H_2O$$

$$100 \text{ g } M_2(SO_4)_3 \cdot mH_2O \text{ has } = \frac{18m \times 100}{(342 + 18m)} \text{ g } H_2O$$

$$\% \text{ of } H_2O = \frac{18m \times 100}{(342 + 18m)} = (100 - 8.1 - 43.2) = 48.7$$

$$\text{or} \quad m = 18$$

$$\therefore \text{Formula of hydrated sulphate } M_2(SO_4)_3 \cdot 18H_2O.$$

Problem 26. 1.8 g iron displaces 2.04 g copper from $CuSO_4$ solution. If equivalent weight of Cu = 31.7, what is equivalent weight of iron? (MLNR 1980)

$$\text{Solution.} \quad \text{Equivalent of Fe} = \text{Equivalent of Cu}$$

$$\frac{W}{E} = \frac{2.04}{31.7}$$

$$\text{or} \quad E = \frac{1.8 \times 31.7}{2.04} = 27.97$$

$$\therefore \text{Equivalent wt. of Fe} = 27.97.$$

PROBLEMS FOR PRACTICE

1. What is the percentage of sulphur in cuprous sulphide, Cu_2S ? ($\text{Cu} = 63.5$, $\text{S} = 32$ amu).
2. What is the mass percentage of iodine in ferric iodide, FeI_3 ? ($\text{Fe} = 56$, $\text{I} = 127$ amu).
3. What is the mass % Ca, mass % N and mass % O in calcium nitrate, $\text{Ca}(\text{NO}_3)_2$? ($\text{Ca} = 40$, $\text{N} = 14$, $\text{O} = 16$).
4. What is the percentage composition by mass of Ba, O, H and water in $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$? ($\text{Ba} = 137.3$, $\text{O} = 16$, $\text{H} = 1$).
5. What is the mass percent of each element in sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$? ($\text{Na} = 23$, $\text{S} = 32$, $\text{O} = 16$).
6. What is the percentage composition by mass of benzene, C_6H_6 ?
7. What is the mass % Be in the mineral beryl, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$? ($\text{Be} = 9$, $\text{Al} = 27$, $\text{Si} = 28$).
8. What is the mass percentage composition of each element in pyrazine, $\text{C}_4\text{H}_4\text{N}_2$?
9. A pure sample of phosphorus iodide weighing 4.12 g was found to contain 3.81 g iodine on quantitative analysis. What is the percentage composition of phosphorus and iodine in phosphorus iodide ?
10. A 4.84 g sample of an organic compound is found to contain 1.52 g F and 2.84 g Cl. What is the mass % of C, mass % F and mass % of Cl in the organic compound ?
11. Nicotine is an alkaloid that contains carbon, hydrogen and nitrogen. On burning 0.2025 g of a pure sample of nicotine in oxygen, 0.55 g CO_2 , 0.1575 g H_2O and 0.035 g N_2 are the products of combustion. Calculate the percentage composition of nicotine.
12. An organic acid contains carbon, hydrogen and oxygen. A 0.252 g of the acid on combustion in oxygen produces 0.462 g CO_2 and 0.126 g H_2O . What is the mass % of each element in the compound ?
13. The molecular mass of a bromide of lead is 367 g mol^{-1} . What is the empirical formula of this substance ? ($\text{Pb} = 207$, $\text{Br} = 80$ amu).
14. The molecular mass of a chloride of sulphur is 103 amu. What is the empirical formula of this substance ? ($\text{S} = 32$, $\text{Cl} = 35.5$ amu).
15. What is the empirical formula of an oxide of nitrogen that contains 25.93% N and 74.07% O?
16. What is the empirical formula of a compound that contains 31.9% Ca, 17.2% B and 50.9% O? ($\text{Ca} = 40$, $\text{B} = 11$ amu).
17. What is the empirical formula of the mineral ilmenite that contains 36.8% Fe, 31.6% Ti and 31.6% O ? ($\text{Fe} = 56$, $\text{Ti} = 48$, $\text{O} = 16$).
18. A given compound contains 0.64 g sulphur and 0.71 g chlorine. What is the simplest formula of the chloride ?
19. A 2.0 g sample of a sulphide of chromium contains 1.04 g chromium. If the molecular mass of the compound is 200, what is its molecular formula ?
20. A 6.75 g sample of metal M on burning in nitrogen yields 10.25 g of the nitride. If the atomic mass of the metal is 27 amu, what is the simplest formula of the nitride?

21. A sample of iron oxide contains 1.677 g iron and 0.64 g oxygen. What is the simplest formula of the oxide ? On heating the sample in excess oxygen, its weight increased to 2.395 g. What is the formula of the new oxide ?
22. A 0.36 g sample of an oxide of iron was heated in a stream of hydrogen until it was reduced completely to metal. If the mass of iron obtained is 0.28 g, what is the formula of the oxide ? (Fe = 56, O = 16).
23. 1.27 g of non-metal (X) reacts with 0.95 g fluorine to form 2.22 g XF_3 . If the atomic mass of fluorine is 19 amu, what is the atomic mass of the element, X ?
24. A compound contains 85.8% boron and 14.2% hydrogen. If its molecular mass is 63 g/mol, what is its molecular formula ?
25. A 5.316 g sample of a compound contains 2.117 g Cu, 1.066 g S and 2.133 g O. The approximate molecular mass of the compound is 159.5 amu. Calculate the molecular formula of the compound ? Cu = 63.5, S = 32, O = 16.
26. What is the empirical formula of an organic compound that contains 60% C, 13.3% H and rest oxygen ?
27. What is the empirical formula of a compound that contains 71.4% C, 3.75% H, 7.57% N and 17.3% S ?
28. An organic compound contains 41.35% C, 6.89% H and 24.12% N. What is its empirical formula ? If the molecular mass of the compound is 58 amu, what is the molecular formula of the compound ?
29. 0.45 g of an organic compound containing only carbon, hydrogen and nitrogen gave 1.1 g of carbon dioxide and 0.3 g of water. If the approximate molecular mass of the compound is 54 g mol⁻¹, what is the molecular formula of the compound ?
30. The molecular mass of iso-ascorbic acid is 176 amu. Chemical analysis indicates a composition of 40.9% C, 4.55% H and 55.44% O. Calculate the molecular formula of the compound.
31. A 12.2 g sample of α -thiobenzaldehyde contains 8.4 g carbon, 0.6 g hydrogen and 3.2 g sulphur. What is its empirical formula ? If the molecular mass of thiobenzaldehyde is 366.57, what is its molecular formula ?
32. A 0.134 g sample of carotene (provitamin A) on combustion in oxygen gave 0.44 g carbon dioxide and 0.126 g water. The molecular mass of carotene is 536. What is its molecular formula ?
33. The molecular mass of cholesterol is 386.6. Chemical analysis indicates it to contain 83.9% C, 11.9% H and 4.1% O. Find the molecular formula of cholesterol.
34. What is the simplest formula of a compound that consists of 0.25 gram-atom of carbon per gram-atom of chlorine ?
35. What is the formula of a compound that contains 0.20 mol of chromium and 0.60 mol of oxygen ?
36. A given compound consists of 1.51×10^{23} atoms of carbon, 7.53×10^{23} atoms of hydrogen and 1.51×10^{23} atoms of nitrogen. What is its simplest formula ?
37. The molecular mass of aspirin is 180 amu. If it contains 60% carbon and twice as many hydrogen atoms as oxygen atoms, find its molecular formula.

ANSWERS

- | | | | |
|---|--|---|--------------------------------------|
| 1. 20.13% | 2. 87.2% | | |
| 3. 24.4% Ca, 17.1% N, 58.5% O | 4. 43.5% Ba, 50.7% O, 5.8% H, 45.7% H ₂ O | | |
| 5. 29.1% Na, 40.5% S, 30.4% O | 6. 92.3% C, 7.7% H | | |
| 7. 5.03% Be | 8. 60% C, 5% H, 35% N | | |
| 9. 7.5% P, 92.5% I | 10. 9.92% C, 31.4% F, 58.68% Cl | | |
| 11. 74.1% C, 8.6% H, 17.3% N | 12. 50% C, 5.56% H, 44.44% O | | |
| 13. PbBr ₂ | 14. SCl ₂ | 15. N ₂ O ₅ | 16. CaB ₂ O ₄ |
| 17. FeTiO ₃ | 18. SCl | 19. Cr ₂ S ₃ | 20. MN |
| 21. Fe ₃ O ₄ , Fe ₂ O ₃ | 22. FeO | 23. 127 amu | 24. B ₃ H ₉ |
| 25. CuSO ₄ | 26. C ₃ H ₈ O | 27. C ₁₁ H ₇ NS | 28. C ₂ H ₄ NO |
| 29. C ₃ H ₄ N | 30. C ₆ H ₈ O ₆ | 31. C ₇ H ₆ S, C ₂₁ H ₁₈ S ₃ | 32. C ₄₀ H ₅₆ |
| 33. C ₂₇ H ₄₆ O | 34. CCl ₄ | 35. CrO ₃ | 36. CH ₃ N |
| 37. C ₉ H ₈ O ₄ | | | |

The Laws of Chemical Combination

Earlier attempts to understand the nature of matter was to discover weight-weight and weight-volume relationships between the reacting substances. Four such experimental laws were formulated between 1774 and 1803.

1. (a) **The law of conservation of mass (Lavoisier, 1774).** This law states that sum of masses of the reactants is always equal to the sum of the masses of the products or matter can neither be created nor destroyed in the course of a chemical reaction,

For reaction : $A + B \longrightarrow C + D$

if m_1 and m_2 are masses of the reactants A and B respectively; m_3 and m_4 are masses of the products C and D, then

$$m_1 + m_2 = m_3 + m_4$$

A chemical-reaction is a rearrangement of atoms and therefore the number and kind of atoms remain unchanged and there is no change in mass.

(b) **The law of conservation of mass and energy.** This law states that matter can be converted into energy and energy can be converted into matter. Also, the sum of matter and energy transformed is equal to the sum of matter and energy obtained by this transformation. The conversion of mass into energy and vice-versa is quantitatively related and is given by the Einstein relation.

$$E = mc^2$$

where E is energy in Joules, m is mass in kilograms and c is velocity of light ($3 \times 10^8 \text{ m sec}^{-1}$).

The loss or gain of mass by mass-energy conversion in a chemical reaction is too small to be detected by the ordinary methods of chemical analysis. Therefore, the law of conservation of mass and energy holds good for all chemical reactions.

2. **The law of constant composition (Proust, 1779).** A pure compound has the same composition and its every molecule contains the same number of atoms of each kind. Thus, a chemical compound always consists of the same elements combined together in the same fixed proportion by mass. For example, pure carbon dioxide prepared by any method has the same composition. Its each molecule contains one carbon atom and two oxygen atoms; and carbon and oxygen are in the ratio of 12 grams of carbon to 32 grams of oxygen.

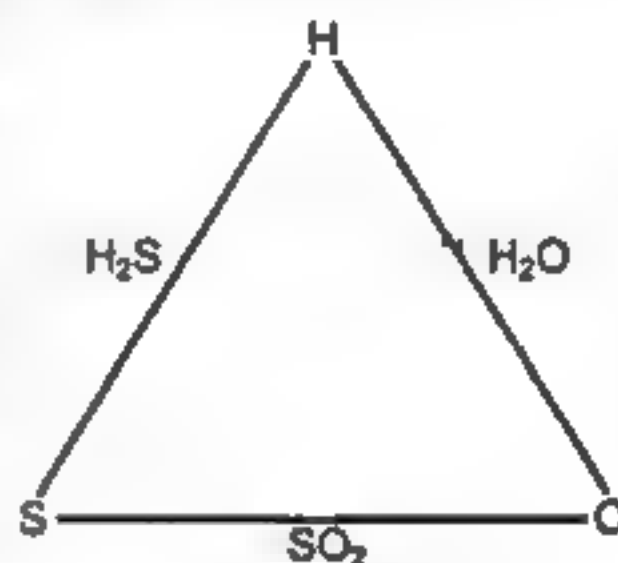
Invalidity of the law of constant composition.

- (a) This law is not true if the same compound is obtained from the isotopes of an element because the mass of each isotope is different.
- (b) This law also does not hold good for non-stoichiometric compounds because they have variable composition.

3. **The law of multiple proportions (Dalton, 1803).** This law states that when two elements A and B combine to form two or more compounds (AB , A_2B , AB_2), the different masses of A that combine with a fixed mass of B (or vice-versa) are in a simple ratio. For example, the masses of oxygen that combine with a fixed mass of nitrogen to form various oxides N_2O , NO , N_2O_3 , N_2O_4 and N_2O_5 are in the simple ratio 1 : 2 : 3 : 4 : 5.
4. **The law of reciprocal proportions (Pichter, 1792).** This law states that if three elements A, B and C combine to form three compounds AB , BC and CA , the ratio of the masses of B and C which combine with a fixed mass of A is either same or simple multiple of the ratio of the masses of B and C when they combine with each other to form BC .

Illustration. Hydrogen, oxygen and sulphur combine to form three compounds, water (H_2O), sulphur dioxide (SO_2) and hydrogen sulphide (H_2S).

- (a) In H_2S , 2g H combines with 32 g S.
In H_2O , 2 g H combines with 16 g O.
- (b) Ratio of masses of S and O that combine with a fixed mass of H (2g).



$$\frac{\text{Mass of S}}{\text{Mass of O}} = \frac{32 \text{ g}}{16 \text{ g}} = \frac{2}{1} \quad \dots(i)$$

- (c) Ratio of masses of S and O when they combine with each other to form SO_2 .

$$\text{In } SO_2, \frac{\text{Mass of S}}{\text{Mass of O}} = \frac{32 \text{ g}}{2 \times 16 \text{ g}} = \frac{32}{32} = \frac{1}{1} \quad \dots(ii)$$

The ratio (i) is double (simple multiple) of ratio (ii) as 2 : 1. This proves the law of reciprocal proportions.

5. **The Gay-Lussac's law of combining volumes.** This law states that when gases combine together at constant pressure and temperature, they do so in volumes which bear a simple ratio to each other and to the volume of the gaseous product.

For the reactions :

| | | | | Ratio of volumes |
|------------|---|-----------|------------------------------|------------------|
| $H_2(g)$ | + | $Cl_2(g)$ | \longrightarrow $2HCl(g)$ | 1 : 1 : 2 |
| 1 volume | | 1 volume | 2 volumes | |
| $N_2(g)$ | + | $3H_2(g)$ | \longrightarrow $2NH_3(g)$ | 1 : 3 : 2 |
| 1 volume | | 3 volume | 2 volumes | |
| $2SO_2(g)$ | + | $O_2(g)$ | \longrightarrow $2SO_3(g)$ | 2 : 1 : 2 |
| 2 volumes | | 1 volume | 2 volumes | |

✓ SOLVED PROBLEMS

Problem 1. What is the mass of carbon that reacts with 28.4 g phosphorus pentoxide to give 28.0 g carbon monoxide and 12.4 g phosphorus, if the law of conservation of mass is true ?



The law of conservation of mass states that the sum of masses of the reactants is equal to the sum of the masses of the products.

$$28.4 \text{ g} + x = 28.0 \text{ g} + 12.4 \text{ g}$$

$$x = 40.4 \text{ g} - 28.4 \text{ g} = 12 \text{ g}$$

Problem 2. The mass of copper oxide obtained by heating 2.16 g metallic copper with nitric acid and subsequent ignition was 2.70 g. In another experiment, 1.15 g of copper oxide on reduction yielded 0.92 g copper. Show that the results illustrate the law of definite proportions.

Solution. (a) Mass of copper oxide = 2.70 g

Mass of copper = 2.16 g

Mass of oxygen = $2.70 - 2.16 = 0.54 \text{ g}$

$$\frac{\text{Mass of copper}}{\text{Mass of oxygen}} = \frac{2.16 \text{ g}}{0.54 \text{ g}} = \frac{4}{1}$$

(b) Mass of copper oxide = 1.15 g

Mass of copper = 0.92 g

Mass of oxygen = $1.15 \text{ g} - 0.92 \text{ g} = 0.23 \text{ g}$

$$\frac{\text{Mass of copper}}{\text{Mass of oxygen}} = \frac{0.92 \text{ g}}{0.23 \text{ g}} = \frac{4}{1}$$

Since the ratio of masses of copper and oxygen in both the cases is the same, the law of definite proportion is justified.

Problem 3. Two oxides of lead were separately reduced to metallic lead by heating in a current of hydrogen and the following data were obtained :

(a) Mass of yellow oxide = 3.45 g

Loss of mass during reduction = 0.24 g

(b) Mass of brown oxide = 1.195 g

Loss of mass during reduction = 0.156 g

Show that the above data illustrate the law of multiple proportions.

Solution. Hydrogen combines with oxygen of the oxide to give metal. Therefore, loss in mass during reduction of the oxide is equal to the mass of oxygen.

(a) Let us fix the mass of oxygen as 1 g.

Mass of oxide = 3.45 g

Mass of oxygen = 0.24 g

Mass of lead = $3.45 \text{ g} - 0.24 \text{ g} = 3.21 \text{ g}$

0.24 g oxygen combines with 3.21 g lead

1 g oxygen combines with $\frac{3.21}{0.24} = 13.4 \text{ g}$ lead

(b) Mass of oxide = 1.195 g

Mass of oxygen = 0.156 g

Mass of lead = $1.195 \text{ g} - 0.156 \text{ g} = 1.039 \text{ g}$

0.156 g oxygen combines with 1.039 g lead

1 g oxygen combines with $\frac{1.039}{0.156} = 6.7 \text{ g}$ lead

The ratio of the masses of lead that combines with a fixed mass of oxygen (1 g) is 6.7 : 13.4 or 1 : 2. This ratio is simple and therefore illustrates the law of multiple proportions.

Problem 4. Hydrogen sulphide contains 94.11% sulphur. Sulphur dioxide contains 50% oxygen. Water contains 11.11% hydrogen. Show that the results are in agreement with the law of reciprocal proportions.

Solution. (a) Calculation of masses of sulphur and oxygen that combine with say 1 g hydrogen.

(i) In H_2S , $100 - 94.11 = 5.89$ g hydrogen combines with 94.11 g sulphur.

1 g hydrogen combines with $\frac{94.11}{5.89} = 15.98$ g of S

(ii) In H_2O , 11.11 g hydrogen combines with $100 - 11.11 = 88.89$ g O.

1 g hydrogen combines with $\frac{88.89}{11.11} = 8$ g oxygen

(b) Calculation of ratio of the masses of S (in H_2S) and O (in H_2O).

$$\frac{\text{Mass of sulphur}}{\text{Mass of oxygen}} = \frac{15.98}{8} = 2 \quad \dots(i)$$

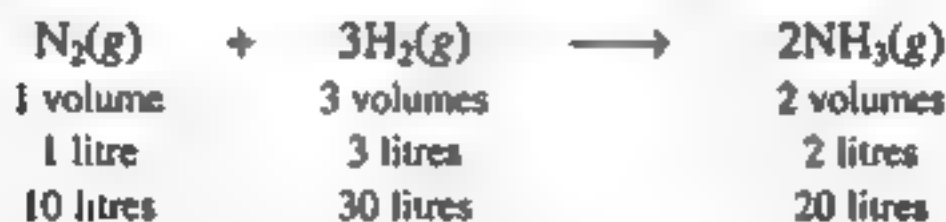
(c) Calculation of the ratio of masses of sulphur and oxygen when they combine to form sulphur dioxide.

$$\frac{\text{Mass of sulphur}}{\text{Mass of oxygen}} = \frac{50}{50} = 1 \quad \dots(ii)$$

The ratio (i) is double of (ii), i.e., 2 : 1. This illustrates the law of reciprocal proportions.

Problem 5. 10 litres of nitrogen gas and 10 litres of hydrogen gas are introduced into an evacuated flask of 10 litres capacity. It is then heated to 700 K and 3 atm pressure. What volume of ammonia is produced?

Solution. Following is the equation for the reaction :



According to the Gay-Lussac's law of combining volumes, 10 litres N_2 combine with 30 litres hydrogen to produce 20 litres ammonia. Since volume of hydrogen in the flask is only 10 litres, therefore, only a part of nitrogen reacts with hydrogen.

According to the equation,

3 volumes hydrogen produces 2 volumes ammonia

\therefore 10 litres hydrogen produces $\frac{2}{3} \times 10 = 6.6$ litres ammonia.

PROBLEMS FOR PRACTICE

- 6 g carbon combines with 16 g oxygen to form 22 g carbon dioxide. Show that these data illustrate the law of conservation of mass.
- 1 g hydrogen was combined with a certain volume of oxygen at STP to form 9 g water. What was the volume of oxygen used up at STP ?
- Show that the data given below for ferric oxide is in agreement with the law of constant composition.

| | (a) | (b) | (c) |
|--------------------|----------|----------|----------|
| Mass of iron | 2.7812 g | 3.0499 g | 4.4913 |
| Mass of iron oxide | 3.9756 g | 4.3596 g | 6.4202 g |

- Two oxides of phosphorus contain 43.64% and 56.33% oxygen respectively. Show that the data illustrate the law of multiple proportions.
- Three oxides of nitrogen contain 63.6%, 46.7 and 30.4% nitrogen respectively. Show that these figures illustrate the law of multiple proportions.
- 12.7 g of chloride of iron gave 2.87 g of silver chloride and 16.25 g of another chloride of it gave 43.05 g of silver chloride. Show that the results illustrate the law of multiple proportions. ($\text{Ag} = 108$, $\text{Fe} = 56$, $\text{Cl} = 35.5$).
- Carbon combines with hydrogen to form three compounds *A*, *B* and *C*. The percentage of hydrogen in *A*, *B* and *C* is 25, 14.3 and 7.7 respectively. (i) Find the empirical formula of the compounds. (ii) Which law of chemical combination does this example illustrate?
- A metal (*X*) has two chlorides containing 44.1% and 34.5% Cl respectively. Calculate the weight of *X* which combines with 35.5 g of chlorine in each compound.
- Two elements *X* and *Y* combine with each other to form three compounds having 75.0%, 85.8% and 92.31% of *X*. Show that these results are in accordance with the law of multiple proportions.
- An oxide of chlorine yields 37 g of HCl and 36 g of H_2O . Calculate the empirical formula of the oxide.
- 0.14 g of an element *A* combines with 0.16 g of the element *B*; also 0.05 g of another element *C* combines with 0.35 g of *A*. Again it is found that 0.2157 g of *C* combines with 2.2857 g of *B*. Show that the results are in agreement with the law of equivalent (reciprocal) proportions.
- Hydrogen sulphide (H_2S) contains 5.86% of hydrogen. Water contains 11.11% of hydrogen, sulphur dioxide contains 50% of oxygen. Show that these figures illustrate the law of reciprocal proportions.
- Show that the following figures illustrate a law of chemical combination : 2.7 g Al reacts with 1.4 g nitrogen to form 4.1 g AlN. 5.4 g Al reacts with 4.8 g oxygen to form 10.2 g Al_2O_3 . 14 g nitrogen combines with 16 g oxygen to form 30 g NO.
- Phosphorus (P_4) combines with hydrogen to give PH_3 . If at a given temperature and pressure 1.0 litre of P_4 produces 4.0 litres of PH_3 , calculate the volume of hydrogen consumed in the reaction.

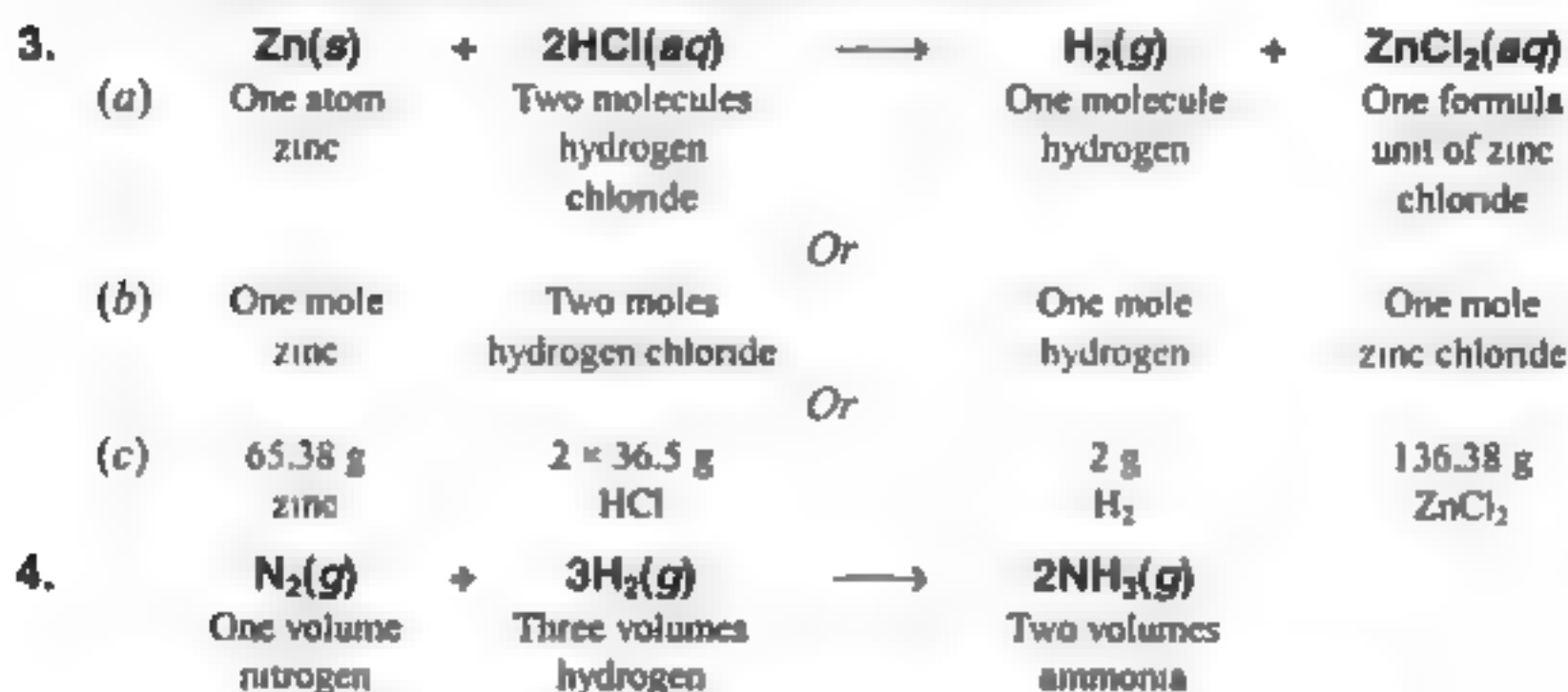
15. Two gaseous elements A and B combine to form two gaseous compounds C and D in two different ways. In one experiment 2 volumes of A and 12 volumes of B react to give 2 volumes of C . In another experiment, 1 volume of A combines with 10 volumes of B to produce 4 volumes of D . Calculate the molecular formulae of A , B , C and D respectively.

ANSWERS

- | | | | |
|-----------------|----------------|---|---|
| 1. 22 g = 22 g | 2. 11.2 litres | 3. $\text{Fe/O} = 2.33$ | 4. 3 : 5 |
| 5. 1 : 2 : 4 | 6. 2 : 3 | 7. (i) CH_4 , CH_2 , CH (ii) 4 : 2 : 1, Multiple | |
| 8. 28 g, 18.7 g | 9. 1 : 2 : 4 | 10. ClO_2 | 11. 1 : 1 |
| 12. 1 : 1 | 13. 7 : 5 | 14. 6 litres | 15. A_4 , B_2 , AB_6 , AB_5 |

Chemical-Equations and Quantitative Relations

- 1. Chemical equation.** It is an expression that indicates the action of chemicals on each other and is so a shorthand notation for writing chemical reactions.
- 2. Informations provided by a balanced chemical equation :**
 - (a) The substances (reactants) taking part in the reaction.
 - (b) The substances (products) formed in the reaction.
 - (c) The relative number of each kind of atoms and molecules.
 - (d) The relative masses of the reactants and products.
 - (e) The relative volumes of gaseous reactants and products.
 - (f) The physical states of the reactants and products.



- 5. Percentage-composition of elements in their compounds.**

$$\text{Mass \%} = \frac{\text{Mass of part}}{\text{Mass of whole}} \times 100$$

For the compound Fe₂O₃,

$$\text{Mass \% of Fe} = \frac{\text{Mass of Iron}}{\text{Mass of Fe}_2\text{O}_3} \times 100$$

- 6. The yield of a chemical reaction.**

$$\text{Percentage yield} = \% \text{ yield} = \frac{\text{Actual amount of product isolated}}{\text{Theoretical amount of product}} \times 100$$

- 7. 1 mole of a gas occupies 22.4 litres at STP.**

✓ SOLVED PROBLEMS

Problem 1. Ammonia gas is prepared by warming solid ammonium chloride with aqueous sodium hydroxide solution.



- (a) How many grams of NH₄Cl are required for every 30 g NaOH used up?

- (b) How many moles of NaCl will be formed?
 (c) How many grams of ammonia will be evolved?

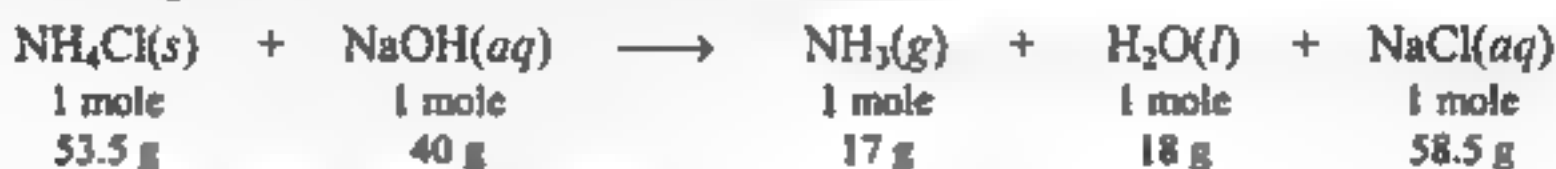
Solution. Molecular mass of NH_4Cl = $14 + 4 \times 1 + 35.5 = 53.5$ amu

Molecular mass of NaOH = $23 + 16 + 1 = 40$ amu

Molecular mass of NH_3 = $14 + 3 \times 1 = 17$ amu

Molecular mass of NaCl = $23 + 35.5 = 58.5$ amu

The balanced equation tells that 1 mole of NH_4Cl reacts with 1 mole of NaOH to form 1 mole of NH_3 gas, 1 mole of H_2O and 1 mole of NaCl .



(a) 40 g NaOH reacts with 53.5 g NH_4Cl

$$30 \text{ g NaOH reacts with } \frac{53.5 \text{ g}}{40 \text{ g}} \times 30 \text{ g} = 40.125 \text{ g } \text{NH}_4\text{Cl}$$

(b) $30 \text{ g NaOH} = \frac{30 \text{ g}}{40 \text{ g/mol}} = 0.75 \text{ moles NaOH}$

0.75 moles NaOH will form 0.75 mole NaCl

(c) 40 g NaOH evolves 17 g NH_3 .

$$30 \text{ g NaOH evolves } \frac{17 \text{ g}}{40 \text{ g}} \times 30 \text{ g} = 12.75 \text{ g } \text{NH}_3.$$

Problem 2. Liquid benzene burns in oxygen according to the following equation:



The density of liquid benzene at 20°C is 0.88 g cm^{-3} . A sample of 4.4 ml of benzene reacts, completely with oxygen.

- (a) What is the mass in grams of water formed?
 (b) How many moles of CO_2 are evolved?
 (c) How many litres of O_2 gas at STP are needed to complete the combustion of benzene?

Solution. Molecular-mass of benzene = $6 \times 12 + 6 \times 1 = 78$ amu

Mass of 4.44 ml of benzene = $4.44 \text{ ml} \times 0.88 \text{ g ml}^{-1} = 3.9072 \text{ g}$

$$3.9072 \text{ g benzene} = \frac{3.9072 \text{ g}}{78 \text{ g/mol}} = 0.05 \text{ mol benzene}$$



(a) 156 g benzene forms 108 g H_2O

$$3.9072 \text{ g benzene forms } \frac{108 \text{ g}}{156 \text{ g}} \times 3.9072 \text{ g} = 2.71 \text{ g } \text{H}_2\text{O}$$

(b) 2 moles benzene evolve 12 moles CO_2

$$0.05 \text{ mole benzene evolves } \frac{12 \text{ mol}}{2 \text{ mol}} \times 0.05 \text{ mol} = 0.3 \text{ mol } \text{CO}_2$$

(c) 2 moles benzene reacts with 15 moles O_2

$$0.05 \text{ mole benzene reacts with } \frac{15 \text{ mol}}{2 \text{ mol}} \times 0.05 \text{ mol} = 0.375 \text{ mol } CO_2$$

1 mole O_2 occupies 22.4 litres at STP.

$$\begin{aligned} \text{Litres of } O_2 \text{ needed for complete combustion} &= 22.4 \text{ litres/mole} \times 0.375 \text{ mole} \\ &= 8.4 \text{ litres } O_2. \end{aligned}$$

Problem 3. Sulphur deposits form in nature when volcanic vapours containing sulphur dioxide and hydrogen sulphide react according to :



(a) How many litres of gas (both SO_2 and H_2S) at STP were needed to form 48 g of sulphur deposit?

(b) How many H_2O molecules are formed ?

$$\text{Solution. } 48 \text{ g sulphur} = \frac{48 \text{ g}}{32 \text{ g/mol}} = 1.5 \text{ moles sulphur}$$



(a) 3 moles of sulphur are produced from 3 moles of the gas (1 mole of SO_2 and 2 moles of H_2S).

$$1.5 \text{ moles of sulphur is produced from } \frac{3 \text{ mol}}{3 \text{ mol}} \times 1.5 \text{ mol} = 1.5 \text{ moles of the gas}$$

1 mole of a gas occupies 22.4 litres at STP

$$1.5 \text{ mole of a gas occupies } 22.4 \times 1.5 = 33.6 \text{ litres}$$

(b) Formation of 3 moles S forms 2 moles H_2O

$$\text{Formation of 1.5 moles S forms } \frac{2 \text{ mol}}{3 \text{ mol}} \times 1.5 \text{ mol} = 1.0 \text{ mol } H_2O$$

$$1 \text{ mol } H_2O = 6.023 \times 10^{23} \text{ } H_2O \text{ molecules.}$$

Problem 4. Mixing of aqueous solutions containing equimolar amounts of barium chloride and sodium sulphate produces a white precipitate of barium sulphate and a solution of sodium chloride remains :

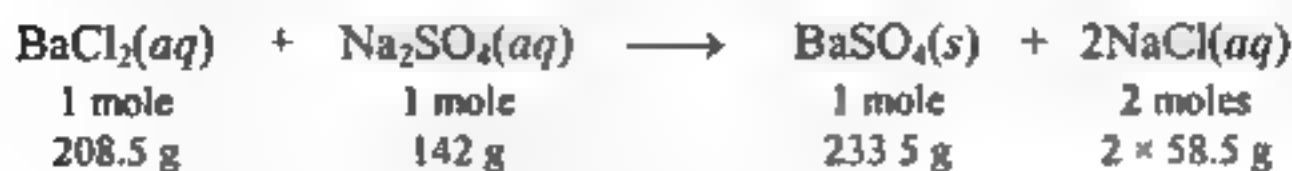
(a) How many grams each of $BaCl_2$ and Na_2SO_4 are required in order to form 4.2 g $BaSO_4$?

(b) How many moles of $NaCl$ are formed ?

$$\text{Solution. Molecular mass of } BaCl_2 = 137.5 + 2 \times 35.5 = 208.5 \text{ amu}$$

$$\text{Molecular mass of } Na_2SO_4 = 2 \times 23 + 32 + 4 \times 16 = 142 \text{ amu}$$

$$\text{Molecular mass of } BaSO_4 = 137.5 + 32 + 4 \times 16 = 233.5 \text{ amu}$$

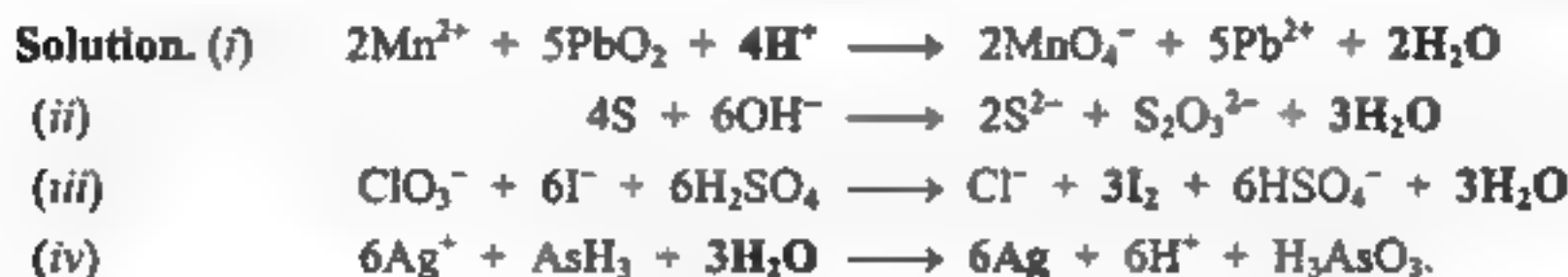


(a) 233.5 g $BaSO_4$ is formed from 208.5 g $BaCl_2$

$$4.2 \text{ g } BaSO_4 \text{ is formed from } \frac{208.5 \text{ g}}{233.5 \text{ g}} \times 4.2 \text{ g} = 3.75 \text{ g } BaCl_2$$

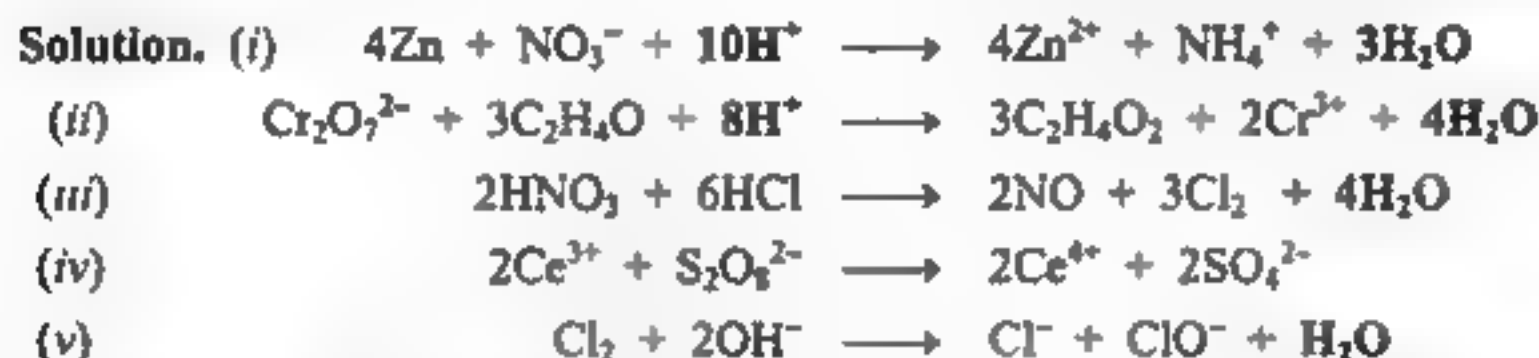
Problem 12. Complete and balance the following reactions that occurs in acidic medium.

- (i) $\text{Mn}^{2+} + \text{PbO}_2 \longrightarrow \text{MnO}_4^- + \text{H}_2\text{O}$
 (ii) $\text{S} + \text{OH}^- \longrightarrow \text{S}^{2-} + \text{S}_2\text{O}_3^{2-}$
 (iii) $\text{ClO}_3^- + \text{I}^- + \text{H}_2\text{SO}_4 \longrightarrow \text{Cl}^- + \text{HSO}_4^-$
 (iv) $\text{Ag}^+ + \text{AsH}_3 \longrightarrow \text{H}_3\text{AsO}_3 + \text{H}^+$ (IIT/JEE 1986)



Problem 13. Complete and balance the following reactions that occurs in acidic medium

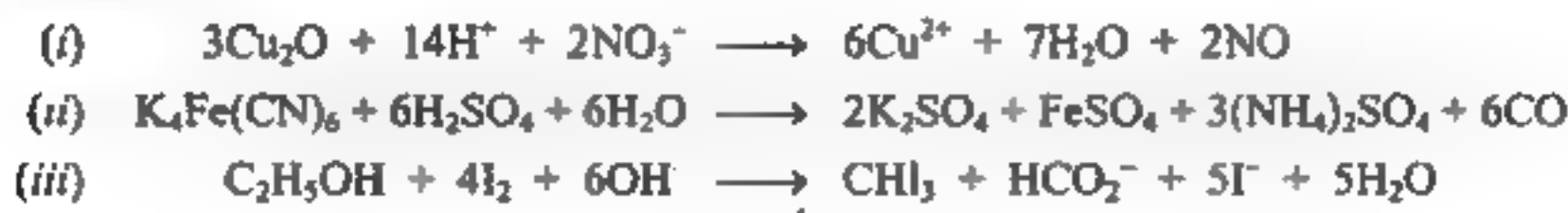
- (i) $\text{Zn} + \text{NO}_3^- \longrightarrow \text{Zn}^{2+} + \text{NH}_4^+$
 (ii) $\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{H}_4\text{O} \longrightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{Cr}^{3+}$
 (iii) $\text{HNO}_3 + \text{HCl} \longrightarrow \text{NO} + \text{Cl}_2$
 (iv) $\text{Ce}^{3+} + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{SO}_4^{2-} + \text{Ce}^{4+}$
 (v) $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}^-$ (Basic medium) (IIT/JEE 1983)



Problem 14. Balance the following equations : (IIT/JEE 1981)

- (i) $\text{Cu}_2\text{O} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{Cu}^{2+} + \text{NO} + \text{H}_2\text{O}$
 (ii) $\text{K}_4\text{Fe}(\text{CN})_6 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO}$
 (iii) $\text{C}_2\text{H}_5\text{OH} + \text{I}_2 + \text{OH}^- \longrightarrow \text{CHI}_3 + \text{HCO}_2^- + \text{I}^- + \text{H}_2\text{O}$

Solution.



PROBLEMS FOR PRACTICE

1. What are the oxidation numbers of Mn in each of the following :

| | | |
|------------------------------|-----------------------------|---------------------|
| (a) MnO_2 | (b) MnCl_2 | (c) KMnO_4 |
| (d) K_2MnO_4 | (e) Mn_2O_7 | |
2. What is the oxidation number of Fe in Fe_3O_4 ?
3. What is the oxidation number of Br in BrF_3 ?
4. Indicate the oxidation state of the element underlined in each of the following :

| | | |
|--|---|--|
| (a) $\underline{\text{Cl}}\text{O}_2\text{Cl}_2$ | (b) $\text{Na}_2\underline{\text{S}}_2\text{O}_3$ | (c) $\underline{\text{I}}\text{Cl}_3$ |
| (d) $\underline{\text{As}}\text{O}_3^{3-}$ | (e) $\underline{\text{I}}\text{O}_4^-$ | (f) $\underline{\text{Sn}}\text{S}_3^{2-}$ |
5. Indicate the valency of nitrogen in the following compounds :

| | | |
|--------------------------|----------------------------|----------------------------|
| (a) N_2O | (b) NO | (c) N_2O_5 |
| (d) NO_2 | (e) N_2O_3 | (f) N_2 |
6. Indicate the oxidation number of nitrogen in each of the following :

| | | |
|--------------------|----------------------------|----------------------------|
| (a) HNO_2 | (b) NO_2^- | (c) NO_3^- |
| (d) HNO_3 | (e) N_2H_4 | (f) NH_2OH |
| (g) NaN_3 | | |
7. Complete and balance the following equations :

| |
|--|
| (a) $\text{H}_2\text{S} + \text{HNO}_3 \longrightarrow \text{NO} + \text{S} + \dots$ |
| (b) $\text{Cr}(\text{OH})_3 + \dots + \text{IO}_3^- \longrightarrow \text{CrO}_4^{2-} + \text{I}^- + \dots$ (basic) |
| (c) $\text{Fe} + \dots + 3\text{O}_2 \longrightarrow 4\text{Fe}^{3+} + \dots$ (acidic) |
| (d) $\text{IO}_3^- + \text{Cl}^- + \dots \longrightarrow \text{I}_2 + 5\text{Cl}_2 + \dots$ (acidic) |
| (e) $\text{H}_2\text{O} + \text{H}_2\text{SO}_3 + \text{I}_3^- \longrightarrow \text{HSO}_4^- + \text{I}^- + \dots$ (acidic) |
| (f) $\text{Cr} + \text{O}_2 + \dots \longrightarrow 4\text{Cr}(\text{OH})_4$ (basic) |
| (g) $\text{OH}^- + \dots + \text{S}_2\text{O}_3^{2-} + \text{MnO}_2 \longrightarrow \text{Mn}(\text{OH})_4 + \text{SO}_4^{2-}$ |
| (h) $\text{I}^- + \text{Cu}^{2+} \longrightarrow \text{I}_2 + \text{CuI}$ |
| (i) $\text{BrO}_3^- + \text{I}^- \longrightarrow \text{Br}^- + \text{OI}^-$ |
| (j) $\text{HNO}_2 + \text{H}^+ + \text{I}^- \longrightarrow \text{I}_3^- + \text{NO} + \dots$ (acidic) |
| (k) $\text{As}_2\text{S}_3 + \text{Fe} \longrightarrow \text{As} + \text{FeS}$ |
| (l) $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}_3^- + \dots$ (basic) |
8. Complete and balance the following equations :

| |
|---|
| (a) $\text{ClO}_2 + \dots \longrightarrow \text{ClO}_2^- + \text{ClO}_3^- + \dots$ (basic) |
| (b) $\text{KMnO}_4 + \text{H}_2\text{S} \longrightarrow \text{MnS} + \text{S} + \text{K}_2\text{SO}_4 + \dots$ (Neutral solution) |
| (c) $\text{MnO}_4^- + \dots + 5\text{H}_2\text{S} \longrightarrow 2\text{Mn}^{2+} + \dots + \text{H}_2\text{O}$ (acidic) |
| (d) $\text{Cr}_2\text{O}_7^{2-} + \text{Cl}^- + 6\text{H}^+ \longrightarrow \text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O}$ |
| (e) $\text{Cr}_2\text{O}_7^{2-} + \text{Sn}^{2+} + \dots \longrightarrow 2\text{Cr}^{3+} + 3\text{Sn}^{4+} + \dots$ (acidic) |
| (f) $\text{KClO}_3 \longrightarrow \text{KClO}_4 + \text{KCl}$ |
| (g) $\dots + \text{SO}_2 \longrightarrow \text{SO}_3^{2-} + \dots$ (basic) |
| (h) $\dots + \text{SO}_3^{2-} + \text{SO}_2 \longrightarrow 2\text{HSO}_3^-$ |
| (i) $\text{As}_4\text{O}_6 + \text{C} \longrightarrow \text{As}_4 + \text{CO}$ |
| (j) $\text{H}_3\text{AsO}_3 + \dots + \text{Zn} \longrightarrow \text{AsH}_3 + \text{Zn}^{2+} + \dots$ (acidic) |

8. (a) $2\text{ClO}_2 + 2\text{OH}^- \longrightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}$
 (b) $2\text{KMnO}_4 + 4\text{H}_2\text{S} \longrightarrow 2\text{MnS} + \text{S} + \text{K}_2\text{SO}_4 + 4\text{H}_2\text{O}$
 (c) $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{S} \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$
 (d) $\text{Cr}_2\text{O}_7^{2-} + 4\text{Cl}^- + 6\text{H}^+ \longrightarrow 2\text{CrO}_2\text{Cl}_2 + 3\text{H}_2\text{O}$
 (e) $\text{Cr}_2\text{O}_7^{2-} + 3\text{Sn}^{2+} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{Sn}^{4+} + 7\text{H}_2\text{O}$
 (f) $4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$
 (g) $2\text{OH}^- + \text{SO}_2 \longrightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$
 (h) $\text{H}_2\text{O} + \text{SO}_3^{2-} + \text{SO}_2 \longrightarrow 2\text{HSO}_3^-$
 (i) $\text{As}_4\text{O}_6 + 6\text{C} \longrightarrow \text{As}_4 + 6\text{CO}$
 (j) $\text{H}_3\text{AsO}_4 + 6\text{H}^+ + 3\text{Zn} \longrightarrow \text{AsH}_3 + 3\text{Zn}^{2+} + 3\text{H}_2\text{O}$
9. (a) $3\text{P} + 5\text{HNO}_3 \longrightarrow 3\text{HPO}_3 + 5\text{NO} + \text{H}_2\text{O}$
 (b) $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} \longrightarrow 2\text{KCl} + 2\text{CrCl}_3 + 7\text{H}_2\text{O} + 3\text{Cl}_2$
 (c) $2\text{C}_3\text{H}_8 + 7\text{O}_2 \longrightarrow 6\text{CO} + 8\text{H}_2\text{O}$
 (d) $\text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{SO}_3 + 5\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{HSO}_4^- + 4\text{H}_2\text{O}$
 (e) $4\text{Fe} + 3\text{O}_2 + 12\text{H}^+ \longrightarrow 4\text{Fe}^{3+} + 6\text{H}_2\text{O}$
 (f) $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{SO}_4^{2-} + 2\text{I}^- + 4\text{H}^+$

ANSWERS

1. (a) +4 ; (b) +2 (c) +7 (d) +6 (e) +7
 2. +2 67 3. +5
 4. (a) +6, (b) +2 (c) +3 (d) +3 (e) +7 (f) +4
 5. (a) +1 (b) +2 (c) +5 (d) +4 (e) +3 (f) 0
 6. (a) +3 (b) +3 (c) +5 (d) +5 (e) -2 (f) -1 (g) -1/3
 7. (a) $3\text{H}_2\text{S} + 2\text{HNO}_3 \longrightarrow 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$
 (b) $2\text{Cr}(\text{OH})_3 + 4\text{OH}^- + \text{IO}_3^- \longrightarrow 2\text{CrO}_4^{2-} + \text{I}^- + 5\text{H}_2\text{O}$
 (c) $4\text{Fe} + 12\text{H}^+ + 3\text{O}_2 \longrightarrow 4\text{Fe}^{3+} + 6\text{H}_2\text{O}$
 (d) $2\text{IO}_3^- + 10\text{Cl}^- + 12\text{H}^+ \longrightarrow \text{I}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O}$
 (e) $\text{H}_2\text{O} + \text{H}_2\text{SO}_3 + \text{I}_3^- \longrightarrow \text{HSO}_4^- + 3\text{I}^- + 3\text{H}^+$
 (f) $4\text{Cr} + 3\text{O}_2 + 4\text{OH}^- + 6\text{H}_2\text{O} \longrightarrow 4\text{Cr}(\text{OH})_4^-$
 (g) $2\text{OH}^- + 3\text{H}_2\text{O} + \text{S}_2\text{O}_3^{2-} + 4\text{MnO}_2 \longrightarrow 4\text{Mn}(\text{OH})_4 + 2\text{SO}_4^{2-}$
 (h) $4\text{I}^- + 2\text{Cu}^{2+} \longrightarrow \text{I}_2 + 2\text{CuI}$
 (i) $\text{BrO}_3^- + 3\text{I}^- \longrightarrow \text{Br}^- + 3\text{OI}^-$
 (j) $2\text{HNO}_2 + 2\text{H}^+ + 3\text{I}^- \longrightarrow \text{I}_3^- + 2\text{NO} + 2\text{H}_2\text{O}$
 (k) $\text{As}_2\text{S}_3 + \text{Fe} \longrightarrow 2\text{As} + 3\text{FeS}$
 (l) $3\text{Cl}_2 + 6\text{OH}^- \longrightarrow 5\text{Cl}^- + \text{ClO}_3^- + 3\text{H}_2\text{O}$

Stoichiometry in Solutions

- 1. Volumetric analysis.** It is a quantitative method of determining the concentration of a solution by titrating it with a solution of known concentration.
- 2. Equivalence or end-point.** In volumetric analysis, a known volume of a solution is taken in a clean glass-vessel such as conical flask. To this is added another solution of a substance little at a time from the burette until the reaction is complete. This stage at which the substances have reacted in stoichiometrically equivalent quantities is called the *end-point*. It is detected by adding a suitable substance known as *indicator* to the solution in a conical-flask before or during titration. Its colour changes when the reaction is just complete.
- 3. Molarity of the solution (M).** It is the number of moles of the substance per litre of the solution.

$$(a) \quad \text{Moles of substance} = \frac{\text{Mass of substance in grams}}{\text{Molecular mass}}$$

$$(b) \quad \text{Molarity} = \frac{\text{Moles of substance}}{\text{Volume of solution in litre}}$$

$$(c) \quad \text{Moles of a substance in solution} = \text{Molarity} \times \text{Volume of solution in litres}$$

$$\text{Millimoles of substance in solution} = \text{Molarity} \times \text{Volume in millilitres}$$

$$(d) \quad \text{Molarity} = \frac{\text{Millimoles of substance}}{\text{Volume in millilitres}}$$

- 4. Normality (N).** It is the number of equivalents (gram-equivalents) of a substance per litre of the solution.

$$(a) \quad \text{Equivalents} = \frac{\text{Mass of substance in grams}}{\text{Equivalent mass of substance}}$$

$$(b) \quad \begin{aligned} \text{Normality} &= \frac{\text{Equivalents of substance}}{\text{Volume of solution in litres}} \\ &= \frac{\text{Milli-equivalents of a substance}}{\text{Volume of solution in millilitres}} \end{aligned}$$

$$(c) \quad \text{Equivalents of a substance in solution} = \text{Normality} \times \text{Volume of solution in litres.}$$

5. $N = nM$

where N and M are the normality and molarity of a solution; and n is a whole number which is given by mol. mass/equivalent mass.

- 6.**

$$\begin{aligned} 1 \text{ millilitre} &= 1 \text{ mL} = 10^{-3} \text{ litre} \\ 1 \text{ millimole} &= 10^{-3} \text{ mole} \\ 1 \text{ milli-equivalent} &= 10^{-3} \text{ equivalent} \end{aligned}$$

- 7. Principle of equivalence.** In a titration, each equivalent of a substance combines with one equivalent of another substance. *Or at the end-point, the number of equivalents of the standard solution is equal to the number of equivalents of the solution of concentration unknown.*

$$\boxed{N_{\text{unknown}} \times V_{\text{unknown}} = N_{\text{standard}} \times V_{\text{standard}}}$$

$$N_1 V_1 = N_2 V_2$$

- 8. Gram-equivalent mass.** The equivalent-mass of a substance in grams is called gram-equivalent mass.

- 9. Equivalent-mass of an acid.** An equivalent of an acid furnishes 1 mole of H^+ ions in a reaction.

$$\text{Equivalent mass of an acid} = \frac{\text{Molecular mass of acid}}{\text{Number of } H^+ \text{ ions reacted or replaced per molecule}}$$

(a) For the reaction :



$$\begin{aligned} \text{Equivalent mass of monoprotic acid, HCl} &= \frac{\text{Molecular mass of HCl}}{1} \\ &= \frac{36.5}{1} = 36.5 \text{ g/equiv.} \end{aligned}$$

A dibasic or triprotic (polyprotic acids) acid may have different equivalent masses depending upon the number of H^+ ions replaced per molecule of the acid.

For the reaction of H_2SO_4 with a base :



Number of H^+ ions reacted per H_2SO_4 molecule, $n = 1$

$$\begin{aligned} \therefore \text{Equivalent mass of } H_2SO_4 &= \frac{\text{Molecular mass } H_2SO_4}{1} \\ &= \frac{98}{1} = 98 \text{ g/equiv.} \end{aligned}$$

$$N_{H_2SO_4} = 1 \times M_{H_2SO_4}$$



Number of H^+ ions reacted per H_2SO_4 molecule, $n = 2$

$$\begin{aligned} \therefore \text{Equivalent mass of } H_2SO_4 &= \frac{\text{Molecular mass } H_2SO_4}{2} \\ &= \frac{98}{2} = 49 \text{ g/equiv} \end{aligned}$$

Also

$$N_{H_2SO_4} = 2 M_{H_2SO_4}$$

- 10. Equivalent mass of a base.** An equivalent of a base furnishes 1 mole OH^- ions and neutralizes 1 equivalent of an acid (1 mole H^+ ions).

$$\text{Equivalent mass of a base} = \frac{\text{Molecular mass of base}}{\text{Number of } OH^- \text{ ions reacted or replaced per molecule}}$$

(a) For the reaction :



Number of OH^- ions reacted per NaOH molecule, $n = 1$

$$\begin{aligned}\text{Equivalent mass of NaOH} &= \frac{\text{Molecular mass NaOH}}{1} \\ &= \frac{40}{1} = 40 \text{ g/equiv.}\end{aligned}$$

or

$$\begin{aligned}N_{\text{NaOH}} &= 1 \times M_{\text{NaOH}} \\ N_{\text{NaOH}} &= M_{\text{NaOH}}\end{aligned}$$

(b) For the reaction :



Number of OH^- ions furnished per $\text{Ca}(\text{OH})_2$ molecule, $n = 2$

$$\begin{aligned}\text{Equivalent mass of Ca(OH)}_2 &= \frac{\text{Molecular mass Ca(OH)}_2}{2} \\ &= \frac{74}{2} = 37 \text{ g/equiv.}\end{aligned}$$

Also :

$$N_{\text{Ca(OH)}_2} = 2 \times M_{\text{Ca(OH)}_2}$$

11. (a) For the reaction :



1 mole of Na_2CO_3 reacts with 1 equivalent of the acid (1 mole H^+ ions), i.e. $n = 1$

$$\begin{aligned}\therefore \text{Equivalent mass of Na}_2\text{CO}_3 &= \frac{\text{Molecular mass Na}_2\text{CO}_3}{1} \\ &= \frac{106}{1} = 106 \text{ g/equiv.}\end{aligned}$$

Also :

$$\begin{aligned}N_{\text{Na}_2\text{CO}_3} &= 1 \times M_{\text{Na}_2\text{CO}_3} \\ N_{\text{Na}_2\text{CO}_3} &= M_{\text{Na}_2\text{CO}_3}\end{aligned}$$

(b) For the reaction :



1 mole of Na_2CO_3 reacts with 2 equivalents HCl (2 moles H^+ ions), i.e. $n = 2$

$$\begin{aligned}\text{Equivalent mass of Na}_2\text{CO}_3 &= \frac{\text{Molecular mass Na}_2\text{CO}_3}{2} \\ &= \frac{106}{2} = 53 \text{ g/equiv.}\end{aligned}$$

Also :

$$N_{\text{Na}_2\text{CO}_3} = 2 \times M_{\text{Na}_2\text{CO}_3}$$

12. Strength of solution in grams/litres.

(a) Strength of solution = Molarity \times Molecular mass

(b) Strength of solution = Normality \times Equivalent mass

13. $N_{\text{acid}} = M_{\text{acid}} \times \text{Basicity of the acid.}$

14. $N_{\text{base}} = M_{\text{base}} \times \text{Acidity of the base.}$

✓ SOLVED PROBLEMS

Problem 1. What is the molarity of a solution made by dissolving 9.8 g of H_2SO_4 in enough water to make 0.400 litre of solution ?

$$\text{Solution. Moles of } \text{H}_2\text{SO}_4 = \frac{\text{Mass of } \text{H}_2\text{SO}_4}{\text{Molecular mass } \text{H}_2\text{SO}_4} = \frac{9.8 \text{ g}}{98 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

$$\text{Molarity of } \text{H}_2\text{SO}_4 = \frac{\text{Moles } \text{H}_2\text{SO}_4}{\text{Volume of solution in litres}} = \frac{0.1 \text{ mol}}{0.4 \text{ litre}} = 0.25 \text{ M}$$

Problem 2. How much oxalic acid should be dissolved per 0.5 litre of solution so that the solution is 0.5 N ?

Solution. Molecular mass of oxalic acid, $\text{COOH} = 90 \text{ amu}$



Number of replaceable H^+ ions per molecule of oxalic acid = 2

$$\text{Equivalent-mass of oxalic acid} = \frac{\text{Molecular mass}}{2} = \frac{90}{2} = 45 \text{ amu}$$

$$\text{Normality of oxalic acid} = \frac{\text{Gram-equivalents}}{\text{Volume in litres}}$$

$$\begin{aligned} \text{Gram-equivalents} &= N_{\text{oxalic acid}} \times V \text{ in litres} \\ &= 0.5 \text{ N} \times 0.5 \text{ litre} = 0.25 \end{aligned}$$

$$\begin{aligned} \text{Mass of oxalic acid} &= \text{Gram-equivalents} \times \text{Equivalent-mass} \\ &= 0.25 \times 45 = 11.25 \text{ g.} \end{aligned}$$

Problem 3. How many millimoles are present in 20 mL of 0.05 M $\text{Ba}(\text{OH})_2$ solution?

$$\begin{aligned} \text{Solution. Milli-moles } \text{Ba}(\text{OH})_2 &= M_{\text{Ba}(\text{OH})_2} \times \text{Volume in mL} \\ &= 0.05 \text{ M} \times 20 \text{ ml} = 1 \text{ millimole.} \end{aligned}$$

Problem 4. What is the normality of a 50 millilitre sample of NaOH solution containing 2.5 milli-equivalents of NaOH ?

$$\text{Solution. } N_{\text{NaOH}} = \frac{\text{Milli-equivalents}}{\text{Millilitres}} = \frac{2.5 \text{ milli-equivalents}}{50 \text{ millilitres}} = 0.05 \text{ N}$$

Problem 5. Phosphoric acid, H_3PO_4 , is a triprotic acid in water. What is the normality of 0.011 M H_3PO_4 as an acid ?

Solution. Since H_3PO_4 contains 3H^+ ions per molecule, its normality is thrice its molarity.



$$\text{Equivalent mass of } \text{H}_3\text{PO}_4 = \frac{\text{Molecular mass of } \text{H}_3\text{PO}_4}{3}$$

$$N = 3 M$$

$$\begin{aligned} N_{\text{H}_3\text{PO}_4} &= 3 \times M_{\text{H}_3\text{PO}_4} \\ &= 3 \times 0.011 = 0.033 \text{ N.} \end{aligned}$$

Problem 6. What is the molarity of 0.04 N Ba(OH)₂ solution?

Solution. Since Ba(OH)₂ contains 2OH⁻ ions per molecule,

$$\text{Equivalent mass of Ba(OH)}_2 = \frac{\text{Molecular mass of Ba(OH)}_2}{2}$$

or $N_{\text{Ba(OH)}_2} = 2 M_{\text{Ba(OH)}_2}$

$$M_{\text{Ba(OH)}_2} = \frac{N_{\text{Ba(OH)}_2}}{2} = \frac{0.04}{2} = 0.02 \text{ M.}$$

Problem 7. What is the equivalent mass of Cr(OH)₃ in the following reaction ? amu of Cr = 52.



Solution. An equivalent of a base furnishes 1 mole OH⁻ ions and neutralizes 1 equivalent of an acid (1 mole H⁺ ions).

Number of OH⁻ ions reacted per Cr(OH)₃ molecule = 3

$$\begin{aligned} \text{Equivalent mass of Cr(OH)}_3 &= \frac{\text{Molecular mass of Cr(OH)}_3}{3} \\ &= \frac{103}{3} = 34.3 \text{ g/equiv.} \end{aligned}$$

Problem 8. What is the final concentration of a solution made by mixing 25 mL of 0.2 M H₂SO₄, 35 mL of 0.25 M H₂SO₄ and 45 mL of 0.35 M H₂SO₄ ?

Solution. Moles of H₂SO₄ in 25 mL of 0.2 M H₂SO₄ = M × V in litres

$$= 0.2 \text{ M} \times \frac{25}{1000} \text{ litres} = 0.005 \text{ mol}$$

$$\text{Moles of H}_2\text{SO}_4 \text{ in 35 mL of 0.25 M H}_2\text{SO}_4 = 0.25 \text{ M} \times \frac{35}{1000} \text{ litres} = 0.00875 \text{ mol}$$

$$\text{Moles of H}_2\text{SO}_4 \text{ in 45 mL of 0.35 M H}_2\text{SO}_4 = 0.35 \text{ M} \times \frac{45}{1000} \text{ litres} = 0.01575 \text{ mol}$$

$$\begin{aligned} \text{Total moles of H}_2\text{SO}_4 &= 0.005 + 0.00875 + 0.01575 \\ &= 0.0295 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Total final volume} &= 25 \text{ mL} + 35 \text{ mL} + 45 \text{ mL} = 105 \text{ mL} \\ &= 0.105 \text{ litre} \end{aligned}$$

$$\begin{aligned} \text{Final concentration} &= \frac{0.0295 \text{ mole H}_2\text{SO}_4}{0.105 \text{ litre of solution}} \\ &= 0.2809 \text{ M H}_2\text{SO}_4. \end{aligned}$$

Problem 9. How much water should be added to 5 litres of 6.0 M NH₃ to make a solution of 2.0 M NH₃ ?

Solution. Moles of NH₃ = 6.0 M × 5 litres = 30 mol

$$\text{Total volume of 2.0 M NH}_3 = \frac{\text{Moles NH}_3}{\text{Molarity NH}_3} = \frac{30 \text{ mol}}{2.0 \text{ M}} = 15 \text{ litres}$$

$$\begin{aligned} \therefore \text{Volume of water to be added to 5 litres of 6.0 M NH}_3 \\ = 15 - 5 = 10.0 \text{ litres.} \end{aligned}$$

Problem 10. 20 millilitres of dilute HNO_3 is neutralized completely with 25 mL of 0.08 M NaOH.

- (a) What is the molarity of HNO_3 ?
 (b) What is the normality of HNO_3 ?

Solution. Moles NaOH used = $0.08 \text{ M} \times \frac{25}{1000} \text{ litre} = 0.002 \text{ mol}$

Since 1 mole of HNO_3 is neutralized by 1 mole of NaOH,

Moles of HNO_3 present in 20 mL = 0.002 mol HNO_3

$$M_{\text{HNO}_3} = \frac{0.002 \text{ mol HNO}_3}{(20/1000) \text{ litre}} = 0.1 \text{ M HNO}_3$$

As HNO_3 furnishes 1 H^+ ion per molecule

$$N_{\text{HNO}_3} = M_{\text{HNO}_3} = 0.1 \text{ N HNO}_3.$$

Problem 11. A 25 mL sample of dil. H_2SO_4 is titrated with 0.5 M NaOH using phenolphthalein as the indicator. It takes 20 ml of the base to reach the end-point at which both the protons of H_2SO_4 are neutralized.

- (a) What is the molarity of H_2SO_4 ?
 (b) What is the normality of H_2SO_4 ?

Solution. Millimoles of NaOH used = $M_{\text{NaOH}} \times V_{\text{NaOH}}$ in mL
 $= 0.5 \text{ M} \times 20 \text{ ml} = 10 \text{ millimol}$

Since two protons are titrated per H_2SO_4 molecule,



\therefore Millimoles of H_2SO_4 used = $\frac{1}{2}$ millimoles of NaOH = $\frac{1}{2} \times 10 = 5 \text{ millimol}$

$$M_{\text{H}_2\text{SO}_4} = \frac{\text{Millimoles}}{V \text{ in mL}} = \frac{5 \text{ millimoles}}{25 \text{ mL}} = 0.2 \text{ M H}_2\text{SO}_4.$$

$$\text{Equivalent mass of H}_2\text{SO}_4 = \frac{\text{Molecular mass of H}_2\text{SO}_4}{2}$$

$$N_{\text{H}_2\text{SO}_4} = 2 M_{\text{H}_2\text{SO}_4} = 2 \times 0.2 = 0.4 \text{ N H}_2\text{SO}_4.$$

Problem 12. How many millilitres of 0.02 N $\text{Ca}(\text{OH})_2$ would be required to neutralize completely 25 mL of 0.05 N H_2SO_4 ?

Solution. Applying normality equation :

$$N_1 V_1 = N_2 V_2$$

$$N_{\text{Ca}(\text{OH})_2} \times V_{\text{Ca}(\text{OH})_2} = N_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4}$$

$$V_{\text{Ca}(\text{OH})_2} = \frac{N_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4}}{N_{\text{Ca}(\text{OH})_2}} = \frac{0.05 \text{ N} \times 25 \text{ mL}}{0.02 \text{ N}} = 62.5 \text{ mL}.$$

Problem 13. Find the equivalent weight of H_3PO_4 in the reaction :



(H = 1, O = 16, P = 31, Ca = 40).

(IIT/JEE 1982)

Solution. Since 2H^+ ions are reacted per H_3PO_4 molecule

$$\begin{aligned}\text{Equivalent mass of } \text{H}_3\text{PO}_4 &= \frac{\text{Molecular mass of } \text{H}_3\text{PO}_4}{2} \\ &= \frac{3 \times 1 + 31 + 4 \times 16}{2} \text{ g/equiv.} = \frac{98}{2} = 49 \text{ g/equiv.}\end{aligned}$$

Problem 14. How many millilitres of 0.02 M Ca(OH)_2 would be required to neutralize completely 40.0 mL of $0.025 \text{ M H}_3\text{PO}_4$?



Number of H^+ ions reacted per H_3PO_4 molecule = 3

$$\text{Equivalent mass of } \text{H}_3\text{PO}_4 = \frac{\text{Molecular mass of } \text{H}_3\text{PO}_4}{3}$$

$$N_{\text{H}_3\text{PO}_4} = 3 M_{\text{H}_3\text{PO}_4} = 3 \times 0.025 = 0.075 \text{ N}$$

$$\text{Equivalent mass of } \text{Ca(OH)}_2 = \frac{\text{Molecular mass of } \text{Ca(OH)}_2}{2}$$

$$N_{\text{Ca(OH)}_2} = 2 M_{\text{Ca(OH)}_2} = 2 \times 0.02 = 0.04 \text{ N.}$$

Applying normality equation :

$$N_1 V_1 = N_2 V_2$$

$$N_{\text{Ca(OH)}_2} \times V_{\text{Ca(OH)}_2} = N_{\text{H}_3\text{PO}_4} \times V_{\text{H}_3\text{PO}_4}$$

$$V_{\text{Ca(OH)}_2} = \frac{N_{\text{H}_3\text{PO}_4} \times V_{\text{H}_3\text{PO}_4}}{N_{\text{Ca(OH)}_2}}$$

$$= \frac{0.075 \text{ N} \times 40.0 \text{ mL}}{0.04 \text{ N}} = 75 \text{ mL of } \text{Ca(OH)}_2.$$

Problem 15. 10 mL of a Na_2CO_3 solution is neutralized completely by 15 mL of 0.04 N HNO_3 solution. What is the concentration of Na_2CO_3 solution ?



$$N_{\text{Na}_2\text{CO}_3} = \frac{N_{\text{HNO}_3} \times V_{\text{HNO}_3}}{V_{\text{Na}_2\text{CO}_3}}$$

$$= \frac{0.04 \text{ N} \times 15 \text{ mL}}{10 \text{ mL}} = 0.06 \text{ N.}$$



1 molecule of Na_2CO_3 reacts with 2H^+ ions

or 1 mole of Na_2CO_3 reacts with 2 equivalents of HNO_3

$$\text{Equivalent mass of } \text{Na}_2\text{CO}_3 = \frac{\text{Molecular mass of } \text{Na}_2\text{CO}_3}{2}$$

$$= \frac{2 \times 23 + 12 + 3 \times 16}{2}$$

$$= \frac{106}{2} = 53 \text{ g/equiv.}$$

$$\begin{aligned}\text{Strength of Na}_2\text{CO}_3 \text{ solution} &= N_{\text{Na}_2\text{CO}_3} \times \text{Equivalent mass of Na}_2\text{CO}_3 \\ &= 0.06 \times 53 = 3.18 \text{ g/litre.}\end{aligned}$$

Problem 16. A sample of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ weighing 0.62 g is added to 100 mL of 0.1 N sulphuric acid. Will the resulting solution be acidic, basic or neutral? $\text{Na} = 23$; $\text{S} = 32$.
(IIT/JEE 1976)



1 mole of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ reacts with 2 moles H^+ ions (2 equivalents)

$$\begin{aligned}\text{Equivalent mass of Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} &= \frac{\text{Molecular mass of Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}}{2} \\ &= \frac{2 \times 23 + 12 + 3 \times 16 + 18}{2} \\ &= \frac{124}{2} = 62 \text{ g/equiv.}\end{aligned}$$

$$\begin{aligned}\text{Equivalents of Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} &= \frac{\text{Mass of Na}_2\text{CO}_3 \cdot \text{H}_2\text{O in grams}}{\text{Equivalent mass Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}} \\ &= \frac{0.62 \text{ g}}{62} = 0.01 \text{ Equivalents.}\end{aligned}$$

$$\begin{aligned}\text{Equivalents of H}_2\text{SO}_4 \text{ used} &= N_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4} \text{ in litres} \\ &= 0.1 \text{ N} \times \frac{100}{1000} \text{ litres} = 0.01 \text{ Equivalents.}\end{aligned}$$

(Since, Equivalents of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ = Equivalents of H_2SO_4 , the resulting solution will be neutral.)

Problem 17. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. This solution is completely neutralized by 26.7 mL of 0.4 N NaOH. Find the percentage of free SO_3 in the sample solution.
(IIT/JEE 1980)



Since 1 mole SO_3 reacts with 2 moles OH^- ions,

$$\begin{aligned}\text{Equivalent mass of SO}_3 &= \frac{\text{Molecular mass of SO}_3}{2} \\ &= \frac{32 + 3 \times 16}{2} = \frac{80}{2} = 40 \text{ g/equiv.}\end{aligned}$$



Since 2H^+ ions react per H_2SO_4 molecule,

$$\begin{aligned}\text{Equivalent mass of H}_2\text{SO}_4 &= \frac{\text{Molecular mass of H}_2\text{SO}_4}{2} \\ &= \frac{2 \times 1 + 32 + 4 \times 16}{2} = \frac{98}{2} = 49 \text{ g/equiv.}\end{aligned}$$

Let x g SO_3 be present in 0.5 g oleum.

Mass of H_2SO_4 in 0.5 g oleum = $(0.5 - x)$ g

$$\text{Equivalents of H}_2\text{SO}_4 = \frac{0.5 - x}{49}$$

$$\text{Equivalents of SO}_3 = \frac{x}{40}$$

$$\text{Equivalents of NaOH} = 0.4 \text{ N} \times \left(\frac{26.7}{1000} \right) \text{ litres} = 0.01068 \text{ Equivalents}$$

1 gram-equivalent of acids neutralize 1 gram-equivalent of bases

$$\text{Hence, } \frac{x}{40} + \frac{0.5 - x}{49} = 0.01068$$

$$49x + 40 \times 0.5 - 40x = 0.01068 \times 49 \times 40$$

$$9x = 0.9328 \text{ g or } x = 0.103 \text{ g}$$

$$\% \text{ of free SO}_3 = \frac{\text{Mass of SO}_3}{\text{Total mass}} \times 100 = \frac{0.103 \text{ g}}{0.5 \text{ g}} \times 100 = 20.6\%$$

Problem 18. A commercial sample (2.013 g) of NaOH containing Na₂CO₃ as an impurity was dissolved in water to make 250 mL solution. A 10 mL portion of this solution required 20 mL of 0.1 N H₂SO₄ for complete neutralization. Calculate the percentage by weight of Na₂CO₃ in the sample.

Solution. Let the mass of Na₂CO₃ in the given sample be x g.

Mass of NaOH in the given sample = $(2.013 - x)$ g



$$\text{Equivalent mass of NaOH} = \frac{\text{Molecular mass of NaOH}}{1}$$

$$= 23 + 16 + 1 = 40 \text{ g/equiv}$$



$$\text{Equivalent mass of Na}_2\text{CO}_3 = \frac{\text{Molecular mass of Na}_2\text{CO}_3}{2} = \frac{106}{2} = 53 \text{ g/equiv.}$$

$$\text{Gram-equivalents of NaOH in 250 mL solution} = \frac{2.013 - x}{40}$$

$$\text{Gram-equivalents of NaOH in 10 mL solution} = \frac{(2.013 - x) \times 10}{40 \times 250}$$

$$\text{Gram-equivalents of Na}_2\text{CO}_3 \text{ in 250 mL solution} = \frac{x}{53}$$

$$\text{Gram-equivalents of Na}_2\text{CO}_3 \text{ in 10 mL solution} = \frac{x \times 10}{53 \times 250}$$

$$\text{Gram-equivalents of H}_2\text{SO}_4 \text{ in 20 mL solution} = N \times V \text{ litres}$$

$$= 0.1 \times \frac{20}{1000} = 0.002$$

1 Gram-equivalent acid neutralizes 1 gram-equivalent base

$$\therefore \frac{(2.013 - x) \times 10}{40 \times 250} + \frac{10x}{53 \times 250} = 0.002$$

$$13x = 0.689$$

$$x = \frac{0.689}{13} = 0.053 \text{ g}$$

$$\% \text{ Na}_2\text{CO}_3 \text{ in the sample} = \frac{0.053 \text{ g} \times 100}{2.013 \text{ g}} = 2.63 \%$$

Problem 19. A solution contains Na_2CO_3 and NaHCO_3 , 10 mL of the solution requires 2.5 mL of 0.1 M H_2SO_4 for neutralization using phenolphthalein as the indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and NaHCO_3 in one litre of the solution.

(IIT/JEE 1979)

Solution. (a) When phenolphthalein is used as the indicator, the end-point appears when Na_2CO_3 is completely converted into NaHCO_3 .



Since 2H^+ ions are titrated per H_2SO_4 molecule,

$$\text{Equivalent mass of H}_2\text{SO}_4 = \frac{\text{Molecular mass of H}_2\text{SO}_4}{2}$$

$$N_{\text{H}_2\text{SO}_4} = 2M_{\text{H}_2\text{SO}_4} = 2 \times 0.1 = 0.2 \text{ N}$$

(b) When methyl-orange is used as the indicator, the end-point appears when NaHCO_3 (otherwise Na_2CO_3 also if methyl orange added before titration) is completely converted into CO_2 .



Since 2H^+ ions are titrated per H_2SO_4 molecule,

$$\text{Equivalent mass of H}_2\text{SO}_4 = \frac{\text{Molecular mass of H}_2\text{SO}_4}{2}$$

$$N_{\text{H}_2\text{SO}_4} = 2M_{\text{H}_2\text{SO}_4} = 2 \times 0.2 = 0.4 \text{ N}$$

1 mole H^+ ions react with 1 mole NaHCO_3

\therefore Equivalent mass of NaHCO_3 = Molecular mass = 84 g/equiv.

Milli-equivalents of 0.1 M H_2SO_4 used to convert Na_2CO_3 into NaHCO_3 using phenolphthalein as the indicator

$$= N_{\text{H}_2\text{SO}_4} \times V \text{ in mL}$$

$$= 0.2 \text{ N} \times 2.5 \text{ ml} = 0.5 \text{ milli-equivalents.}$$

\therefore Milli-equivalents of 0.4 N H_2SO_4 used to neutralize NaHCO_3 produced from Na_2CO_3 into CO_2

$$= 0.5 \text{ milli-equivalents}$$

Milli-equivalents of 0.4 N H_2SO_4 used to neutralize total NaHCO_3 into CO_2

$$= 0.4 \text{ N} \times 2.5 \text{ mL} = 1.0 \text{ milli-equivalent}$$

Milli-equivalents of 0.4 N H_2SO_4 used to neutralize Na_2CO_3 in the sample solution

$$= 1 - 0.5$$

$$= 0.5 \text{ milli-equivalents}$$

Total milli-equivalents of H_2SO_4 used to neutralize Na_2CO_3 completely

$$= 0.5 + 0.5 = 1.0 \text{ milli-equivalent}$$

As 1 equivalent acid neutralizes 1 equivalent base

Milli-equivalents of Na_2CO_3 in the solution = 1 milli-equivalent

Milli-equivalents of NaHCO_3 in the solution = 0.5 milli-equivalent

$$N_{\text{NaHCO}_3} = \frac{\text{Milli-equivalents}}{V \text{ in ml}} = \frac{1}{10} = 0.1 \text{ N}$$

$$N_{\text{NaHCO}_3} = \frac{0.5}{10} = 0.05 \text{ N}$$

For complete neutralization of Na_2CO_3 with H_2SO_4 ,



$$\text{Equivalent mass of Na}_2\text{CO}_3 = \frac{\text{Molecular mass of Na}_2\text{CO}_3}{2} = \frac{106}{2} = 53 \text{ g/equiv.}$$

$$\text{Strength} = \text{Normality} \times \text{Equivalent-mass}$$

$$\text{Strength of Na}_2\text{CO}_3 = 0.1 \text{ N} \times 53 = 5.3 \text{ g/litre}$$

$$\text{Strength of NaHCO}_3 = 0.05 \text{ N} \times 84 = 4.2 \text{ g/litre}$$

Problem 20. An a mL of a solution containing NaOH and Na_2CO_3 requires 20 mL of $\frac{N}{10}$ HCl when titrated using phenolphthalein as the indicator. Another a mL solution of the sample requires 25 mL of the same acid using methyl-orange as the indicator. Calculate the amount of NaOH and Na_2CO_3 in a mL of the solution.

Solution. (a) When phenolphthalein is used as the indicator, end-point appears when NaOH is completely neutralized and Na_2CO_3 is converted into NaHCO_3 .



$$\text{Equivalent mass of NaOH} = \text{Molecular mass of NaOH} = 40 \text{ g/equiv.}$$



(b) When methyl-orange is used as the indicator, end-point appears, when NaOH is completely neutralized and Na_2CO_3 is also completely neutralized.



$$\text{Equivalent mass of Na}_2\text{CO}_3 = \frac{\text{Molecular mass of Na}_2\text{CO}_3}{2} = \frac{106}{2} = 53 \text{ g/equiv.}$$

$$\text{Milli-equivalents of HCl in 20 mL of } \frac{N}{20} \text{ HCl} = \frac{N}{20} \times 20 \text{ mL} = 1 \text{ milli-equivalent}$$

$$\begin{aligned} \text{Milli-equivalents of HCl in 25 mL of } \frac{N}{20} \text{ HCl} &= \frac{N}{20} \times 25 \text{ mL} \\ &= 1.25 \text{ milli-equivalents} \end{aligned}$$

\therefore Milli-equivalents of HCl used in neutralizing NaHCO_3

$$= 1.25 - 1.0 = 0.25 \text{ milli-equivalents}$$

Since 1 mole Na_2CO_3 changes into 1 mole NaHCO_3

Milli-equivalents of HCl used in neutralizing Na_2CO_3 completely

$$= 0.25 + 0.25 = 0.50 \text{ milli-equivalents}$$

Milli-equivalents of HCl used in neutralizing NaOH

$$= 1 - 0.25 = 0.75 \text{ milli-equivalents}$$

As 1 equivalent acid neutralizes 1 equivalent base

$$\text{Milli-equivalents of NaOH} = 0.75$$

$$\text{Milli-equivalents of Na}_2\text{CO}_3 = 0.50$$

$$\text{Amount of NaOH} = \text{Equivalents} \times \text{Equivalent mass}$$

$$= \frac{0.75}{1000} \times 40 = 0.03 \text{ g}$$

$$\text{Amount of Na}_2\text{CO}_3 = \frac{0.5}{1000} \times 53 = 0.0265 \text{ g.}$$

Problem 21. A mixture containing only Na_2CO_3 and K_2CO_3 weighing 1.22 g was dissolved in water to form 100 ml of a solution. 20 ml of this solution required 40 mL of 0.1 N HCl for neutralization. Calculate the weight of Na_2CO_3 in the mixture. If another 20 mL of this solution is treated with excess BaCl_2 , what will be the weight of the precipitate thus obtained. (IIT/JEE 1976)

Solution. Let weight of $\text{Na}_2\text{CO}_3 = x \text{ g}$

$$\text{Weight of K}_2\text{CO}_3 = (1.22 - x) \text{ g}$$

$$\text{Equivalent mass of Na}_2\text{CO}_3 = \frac{\text{Molecular mass Na}_2\text{CO}_3}{2} = \frac{106}{2} = 53 \text{ g/equiv.}$$

$$\text{Equivalent mass of K}_2\text{CO}_3 = \frac{\text{Molecular mass K}_2\text{CO}_3}{2} = \frac{138}{2} = 69 \text{ g/equiv.}$$

$$\text{Gram-equivalents of Na}_2\text{CO}_3 \text{ in 100 mL solution} = \frac{x}{53}$$

$$\text{Gram-equivalents of K}_2\text{CO}_3 \text{ in 100 mL solution} = \frac{1.22 - x}{69}$$

$$\therefore \text{Total gram-equivalents in 100 mL solution} = \frac{x}{53} + \frac{1.22 - x}{69}$$

$$\text{Total gram-equivalents in 20 mL solution} = \left[\frac{x}{53} + \frac{1.22 - x}{69} \right] \times \frac{20}{100}$$

$$\begin{aligned} \text{Gram-equivalents of HCl in 40 mL of 0.1 N HCl} &= 0.1 \text{ N} \times \frac{40}{1000} \text{ litres} \\ &= 0.004 \text{ equivalents} \end{aligned}$$

According to the law of normalities :

$$\left[\frac{x}{53} + \frac{1.22 - x}{69} \right] \times \frac{20}{100} = 0.004$$

$$x = 0.53 \text{ g}$$

$$0.004 \text{ equivalent of HCl} = 0.004 \text{ equivalent CO}_3^{2-}$$

$$= 0.004 \text{ equivalent BaCO}_3$$

$$\begin{aligned}\text{Equivalent mass of BaCO}_3 &= \frac{\text{Molecular mass BaCO}_3}{2} \\ &= \frac{137.5 + 12 + 48}{2} = \frac{197.5}{2} = 98.65 \text{ g/equiv.}\end{aligned}$$

$$\text{Weight of BaCO}_3 \text{ precipitate} = 0.004 \times 98.65 = 0.3946 \text{ g.}$$

Problem 22. Five mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made upto 2 litre. 30 mL of this mixture exactly neutralize 42.9 mL of sodium carbonate solution containing one gram of $\text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}$ in 100 mL of water. Calculate the amount in grams of the sulphate ions in solution. (IIT/JEE 1985)

$$\text{Solution.} \quad N_{\text{H}_2\text{SO}_4} = M_{\text{H}_2\text{SO}_4} \times \text{Basicity} = 17.0 \times 2 = 34 \text{ N}$$

Gram-equivalents of $\text{HNO}_3 + \text{HCl} + \text{H}_2\text{SO}_4$

$$= \frac{8 \times 5}{1000} + \frac{5 \times 4.8}{1000} + \frac{34 \times V}{1000}$$

Gram-equivalents in 30 mL of the solution diluted to 2 litres

$$= \left[\frac{8 \times 5}{1000} + \frac{5 \times 4.8}{1000} + \frac{34 \times V}{1000} \right] \times \frac{30}{2000}$$

$$\text{Equivalent mass of Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O} = \frac{\text{Molecular mass}}{2} = \frac{286}{2} = 143 \text{ g/equiv.}$$

$$\text{Gram-equivalents of Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O in 42.9 mL solution} = \frac{1 \text{ g}}{143 \text{ g}} \times \frac{42.9 \text{ mL}}{100 \text{ mL}} = 0.003$$

\therefore According to the law of normalities,

$$\left[\frac{8 \times 5}{1000} + \frac{5 \times 4.8}{1000} + \frac{34 \times V}{1000} \right] \times \frac{30}{2000} = 0.003$$

$$\frac{5}{1000} [8 + 4.8 + 6.8 V] \times \frac{30}{2000} = 0.003$$

$$12.8 + 6.8 V = 0.003 \times \frac{1000}{5} \times \frac{2000}{30} = 40$$

$$V = \frac{40 - 12.8}{6.8} = \frac{27.2}{6.8} = 4 \text{ mL}$$

$$\text{Molecular mass of SO}_4^{2-} \text{ ion} = 32 + 4 \times 16 = 96 \text{ amu}$$

$$1000 \text{ mL of 1 M H}_2\text{SO}_4 \text{ contains 1 mole SO}_4^{2-} \text{ ions} = 96 \text{ g}$$

$$4 \text{ mL of 17 M H}_2\text{SO}_4 \text{ contains} = \frac{17 \times 4 \times 96}{1000} = 6.528 \text{ g SO}_4^{2-} \text{ ions.}$$

Problem 23. 4.08 g of a mixture of BaO and unknown carbonate MCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 mL of 1 N HCl. The excess acid required 16 mL of 2.5 N NaOH solution for complete neutralization. Identify the metal M. (IIT/JEE 1983)



Mass of mixture of BaO and $\text{MCO}_3 = 4.08 \text{ g}$

Mass of residue = 3.64 g

Mass of CO_2 evolved = $4.08 - 3.64 = 0.44 \text{ g}$

Moles of CO_2 evolved = $\frac{\text{Mass}}{\text{Molecular mass}} = \frac{0.44}{44} = 0.01 \text{ mol}$

Since 1 mole CO_2 is evolved from 1 mole MCO_3 ,

\therefore Moles of MCO_3 present in the mixture = 0.01 mol

Milli-equivalents of HCl in 100 mL of 1 N HCl = $1 \text{ N} \times 100 \text{ mL} = 100$

Milli-equivalents of NaOH in 16 mL of 2.5 N NaOH = $2.5 \text{ N} \times 16 \text{ mL} = 40$

\therefore Milli-equivalents of HCl in excess = 40

Milli-equivalents HCl used in dissolving the mixture of BaO and MO

= $100 - 40 = 60$ milli-equivalents

60 Milli-equivalents = $\frac{60}{1000} = 0.06$ Equivalents



Equivalent mass of MO = $\frac{\text{Molecular mass of MO}}{2}$

\therefore Equivalents of MO in the mixture = $0.01 \times 2 = 0.02$

\therefore Equivalents of BaO in the mixture = $0.06 - 0.02 = 0.04$

Moles of BaO in the mixture = $\frac{0.04}{2} = 0.02 \text{ mol}$

Molecular mass of BaO = $138 + 16 = 154 \text{ amu}$

\therefore Mass of BaO = $0.02 \times 154 = 3.08 \text{ g}$

Mass of MCO_3 = $4.08 - 3.08 = 1 \text{ g}$

0.01 mole MCO_3 weighs = 1 g

1 mole MCO_3 weighs = $\frac{1}{0.01} = 100 \text{ g}$

Molecular mass of MCO_3 = 100 amu

Atomic mass of unknown M = $100 - (\text{C} + 3 \times \text{O})$

= $100 - (12 + 3 \times 16) = 40 \text{ amu}$

\therefore The metal M is Calcium.

Problem 24. Find the equivalent weight of a metal carbonate, 0.84 g of which reacts exactly with 40 mL of N/2 sulphuric acid.

Solution.

Gram-equivalents metal carbonate = Gram-equivalents H_2SO_4 in 40 mL of N/2 H_2SO_4

= $\frac{\text{N}}{2} \times \left(\frac{40}{1000} \right) \text{ litre} = 0.02 \text{ equivalent}$

0.02 Equivalent metal carbonate equals 0.84 g

$$1 \text{ Equivalent metal carbonate equals } = \frac{0.84}{0.02} = 42 \text{ g}$$

\therefore Equivalent weight of metal carbonate is 42 g/equiv.

Problem 25. 1.0 g of a mixture consisting of equal number of moles of carbonates of two alkali metals required 44.4 mL of 0.500 N hydrochloric acid for complete reaction. If the atomic-weight of one of the metals is 7.00, find the atomic weight of the other metal. What will be the total amount of sulphate formed on quantitative conversion of 1.0 g of the mixture into sulphates ? (IIT/JEE 1972)

Solution. Molecular mass of one carbonate M_2CO_3

$$= 2 \times 7 + 12 + 3 \times 16 = 74 \text{ amu}$$

Molecular mass of other carbonate M'_2CO_3

$$= 2 \times a + 12 + 3 \times 16 = 2a + 60 \text{ amu}$$

Equivalents of metal carbonates = Equivalents of HCl in 44.4 mL of 0.5 N HCl

$$= 0.5 \text{ N} \times \frac{44.4}{1000} \text{ litre} = 0.0222$$

$$\text{Equivalent-mass of } M_2CO_3 = \frac{\text{Molecular mass of } M_2CO_3}{2}$$

$$\text{Moles of metal carbonates} = \frac{0.0222}{2} = 0.0111 \text{ mol}$$

$$\text{Moles of each carbonate} = \frac{0.0111}{2} = 0.00555 \text{ mol}$$

$$\begin{aligned} \text{Mass of } M_2CO_3 &= \text{Moles} \times \text{Molecular-mass} \\ &= 0.00555 \times 74 = 0.4107 \text{ g} \end{aligned}$$

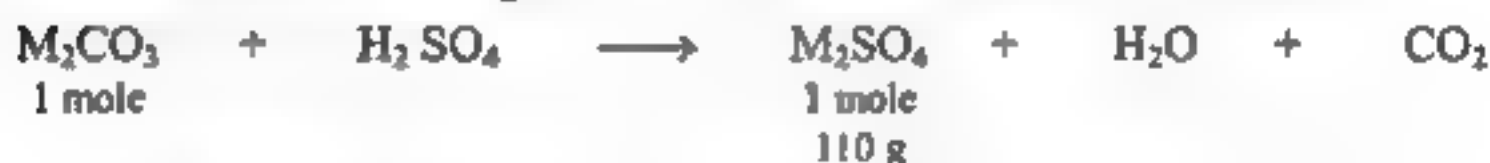
$$\text{Mass of } M'_2CO_3 = 0.00555 \times (2a + 60) \text{ g}$$

Since the mass of the mixture is 1 g,

$$\therefore 0.4107 + 0.00555(2a + 60) = 1$$

$$a = 23.1 \text{ amu}$$

$$\text{Molecular mass of } M'_2SO_4 = 2 \times 7 + 32 + 4 \times 16 = 110 \text{ amu}$$



$$\text{Amount of } M_2SO_4 \text{ formed} = 0.00555 \times 110 = 0.6105 \text{ g}$$



$$\text{Amount of } M'_2SO_4 \text{ formed} = 0.00555 \times 142.2 = 0.7892 \text{ g}$$

$$\text{Total amount of sulphate formed} = 0.6105 \text{ g} + 0.7892 \text{ g} = 1.4 \text{ g.}$$

Problem 26. 1 gram of a sample of chalk containing calcium sulphate as an impurity is dissolved in 50 mL of 0.5 N HCl. 25 mL of 0.4 N NaOH is required to neutralize the excess acid. What is the percentage purity of the chalk sample ?

Solution. $CaSO_4$ does not react with HCl but $CaCO_3$ dissolves with the liberation of CO_2 .



$$\begin{aligned}\text{Equivalent mass of CaCO}_3 &= \frac{\text{Molecular mass of CaCO}_3}{2} \\ &= \frac{40 + 12 + 3 \times 16}{2} = \frac{100}{2} = 50 \text{ g/equiv.}\end{aligned}$$

$$\text{Milli-equivalents in 50 mL of 0.5 N HCl} = 0.5 \text{ N} \times 50 \text{ mL} = 25$$

$$\text{Milli-equivalents in 25 mL of 0.4 N NaOH} = 0.4 \text{ N} \times 25 \text{ mL} = 10$$

$$\therefore \text{Milli-equivalents of HCl used in reacting with CaCO}_3 = 25 - 10 = 15$$

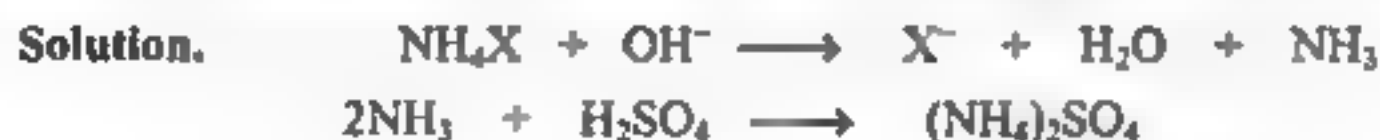
$$15 \text{ milli-equivalents} = \frac{15}{1000} = 0.015 \text{ equivalents}$$

$$\therefore \text{Equivalents of CaCO}_3 \text{ in the sample} = 0.015 \text{ equivalents}$$

$$\begin{aligned}\text{Amount of CaCO}_3 &= 0.015 \text{ equivalents} \times 50 \text{ g/equiv.} \\ &= 0.75 \text{ g CaCO}_3\end{aligned}$$

$$\% \text{ purity of chalk} = \frac{0.75 \text{ g}}{1.00 \text{ g}} \times 100 = 75\%$$

Problem 27. 0.15 g of a sample of an ammonium salt were heated with excess of NaOH solution. The ammonia gas evolved was passed into 75 mL of 0.05 M H₂SO₄. The unreacted acid required 50 mL of 0.1 N NaOH solution for complete neutralization. Calculate the percentage of ammonia and ammonium radical in the sample.



$$\text{Equivalent mass of NH}_3 = \frac{\text{Molecular mass of NH}_3}{1}$$

$$\text{Equivalent mass of H}_2\text{SO}_4 = \frac{\text{Molecular mass of H}_2\text{SO}_4}{2}$$

$$N_{\text{H}_2\text{SO}_4} = 2M_{\text{H}_2\text{SO}_4} = 2 \times 0.05 = 0.1 \text{ N}$$

$$\text{Milli-equivalents of H}_2\text{SO}_4 \text{ in 75 mL of 0.1 N H}_2\text{SO}_4 = 0.1 \text{ N} \times 75 \text{ mL} = 7.5$$

$$\text{Milli-equivalents of NaOH in 50 mL of 0.1 N NaOH} = 0.1 \text{ N} \times 50 \text{ mL} = 5.0$$

$$\text{Milli-equivalents of H}_2\text{SO}_4 \text{ that reacted with NH}_3 = 7.5 - 5.0 = 2.5$$

$$2.5 \text{ milli-equivalents} = \frac{2.5}{1000} = 0.0025 \text{ equivalents}$$

$$\text{Equivalents of NH}_3 \text{ evolved} = 0.0025$$

$$\text{Mass of NH}_3 \text{ evolved} = 0.0025 \times 17 = 0.0425 \text{ g}$$

$$(a) \quad \% \text{ of NH}_3 \text{ in the sample} = \frac{0.0425 \text{ g}}{0.15 \text{ g}} \times 100 = 28.3\%$$

$$(b) \quad \text{NH}_3 \rightleftharpoons \text{NH}_4^+$$

$$\begin{array}{cc} 17 \text{ g} & 18 \text{ g} \end{array}$$

$$\% \text{ of NH}_4^+ \text{ in the sample} = \frac{18 \text{ g}}{17 \text{ g}} \times 28.3\% = 29.96\%$$

Problem 28. 20 mL of HNO_3 requires 25 mL of a $\text{Ba}(\text{OH})_2$ solution for complete neutralization. 20 mL of $\text{Ba}(\text{OH})_2$ solution is neutralized completely by 10 mL of 0.02 M H_2SO_4 . What is the concentration of HNO_3 solution?



$$\text{Equivalent mass of } \text{H}_2\text{SO}_4 = \frac{\text{Molecular mass of } \text{H}_2\text{SO}_4}{2}$$

or $N_{\text{H}_2\text{SO}_4} = 2 \times M_{\text{H}_2\text{SO}_4} = 2 \times 0.02 = 0.04 \text{ N}$

$$N_{\text{Ba}(\text{OH})_2} \times V_{\text{Ba}(\text{OH})_2} = N_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4}$$

$$N_{\text{Ba}(\text{OH})_2} = \frac{N_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4}}{V_{\text{Ba}(\text{OH})_2}} = \frac{0.04 \text{ N} \times 10 \text{ mL}}{20 \text{ mL}} = 0.02 \text{ N}$$

$$N_{\text{HNO}_3} = \frac{N_{\text{Ba}(\text{OH})_2} \times V_{\text{Ba}(\text{OH})_2}}{V_{\text{HNO}_3}}$$

$$= 0.02 \text{ N} \times \frac{25 \text{ mL}}{20 \text{ mL}} = 0.025 \text{ N}$$

$$\begin{aligned} \text{Strength of } \text{HNO}_3 &= \text{Normality} \times \text{Equivalent mass} \\ &= 0.025 \times 63 = 1.575 \text{ g/litre.} \end{aligned}$$

Problem 29. 1.575 g of oxalic acid $(\text{COOH})_2 \cdot x \text{H}_2\text{O}$ are dissolved in water and the volume made up to 250 mL. On titration 16.68 mL of this solution requires 25 mL of N/15 NaOH solution for complete neutralization. Calculate x . (BITS 1987)

Solution. Milli-equivalents of oxalic acid in 16.68 mL

$$= \text{Milli-equivalents of NaOH} = 25 \times \frac{1}{15}$$

$$\begin{aligned} \therefore \text{Milli-equivalents of oxalic acid in 250 mL} &= 25 \times \frac{1}{15} \times \frac{250}{16.68} \\ &= 24.98 \text{ Milli-equivalents} \end{aligned}$$

$$\text{Molarity} \times \text{Volume in cm}^3 = 24.98$$

$$\left[\frac{1.575}{(90 + 18x)} \times \frac{1000}{250} \right] \times 250 = 24.98$$

or

$$x = 2.$$

Problem 30. A small amount of CaCO_3 completely neutralizes 525 mL of N/10 HCl and no acid is left at the end. After converting all calcium chloride to CaSO_4 , how much plaster of paris can be obtained? (Dhanbad 1991)

Solution. Milli-equivalents of CaCO_3 = Milli-equivalents of HCl

Milli-equivalents of CaCl_2 formed

$$= 525 \text{ mL} \times \frac{\text{N}}{10} = 52.5 \text{ Meq.}$$

This CaCl_2 is now converted to CaSO_4 and then to plaster of paris $\left(\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O} \right)$

∴ Milli-equivalents of CaCl_2 formed

= Milli-equivalents of CaSO_4 obtained by this CaCl_2

= Milli-equivalents of $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ or plaster of paris

$$\frac{w}{145/2} \times 1000 = 52.5$$

∴ Let weight of $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ formed be w g

∴ Milli-equivalents of plaster of paris = $\left[\frac{w}{145/2} \times \frac{1000}{525} \right] \times 525 = 52.5$ equiv.

or
$$w = 52.5 \times \frac{145}{2} \times \frac{1}{1000} = 3.81 \text{ g}$$

Problem 31. 25 mL of a solution of Na_2CO_3 having a specific gravity of 1.25 g ml^{-1} required 32.9 mL of a solution of HCl containing 109.5 g of the acid per litre for complete neutralization. Calculate the volume of $0.84 \text{ N H}_2\text{SO}_4$ that will be completely neutralized by 125 g of Na_2CO_3 . (MLNR 1991)

Solution. (i)
$$N_{\text{HCl}} = \frac{109.5}{36.5 \times 1} = 3 \text{ N}$$

Since Na_2CO_3 is completely neutralized by HCl

∴ Milli-equivalents of Na_2CO_3 = Milli-equivalents of HCl

$$N \times 25 \text{ mL} = 32.9 \text{ mL} \times 3 \text{ N}$$

∴
$$N_{\text{Na}_2\text{CO}_3} = \frac{32.9 \times 3}{25} = 3.948 \text{ N}$$

(ii) Weight of Na_2CO_3 solution = 125 g

∴ Volume of Na_2CO_3 solution = $\frac{125 \text{ g}}{1.25 \text{ g/mL}} = 100 \text{ mL}$

∴ Milli-equivalents of H_2SO_4 = Milli-equivalents of Na_2CO_3

$$0.84 \text{ N} \times V = 100 \text{ mL} \times 3.948 \text{ N}$$

∴ Volume of H_2SO_4 required = 470 mL.

Problem 32. 1 g of impure Na_2CO_3 is dissolved in water and the solution is made up to 250 mL. To 50 mL of this made up solution, 50 mL of 0.1 N HCl is added and the mixture after shaking well, required 10 mL of 0.16 N NaOH solution for complete neutralization. Calculate % purity of the sample of Na_2CO_3 . (BITS 1989)

Solution. Milli-equivalents of HCl added to 50 mL Na_2CO_3 solution

$$= 50 \text{ mL} \times 0.1 \text{ N} = 5 \text{ Meq.}$$

Milli-equivalents of HCl left after reaction with 50 mL Na_2CO_3 solution

$$= \text{Milli-equivalents of NaOH used} = 10 \text{ mL} \times 0.16 \text{ N}$$

$$= 1.6 \text{ Milli-equivalents}$$

∴ Milli-equivalents of HCl used for neutralizing Na_2CO_3 in 50 mL solution

$$= 5 - 1.6 = 3.4 \text{ Milli-equivalents}$$

∴ Milli-equivalents of HCl used for Na_2CO_3 in 250 mL solution

$$= \frac{3.4 \times 250}{50} = 17 \text{ Milli-equivalents}$$

Milli-equivalents of HCl = Milli-equivalents of Na_2CO_3 = 17

$$\left[\frac{w}{106/2} \times \frac{1000 \times 250}{250} \right] = 17$$

$$w = 0.901 \text{ g}$$

% of Na_2CO_3 in sample = $\frac{\text{Mass of } \text{Na}_2\text{CO}_3 \text{ in the sample}}{\text{Mass of sample}}$

$$= \frac{0.901 \text{ g}}{1 \text{ g}} \times 100\% = 90.1\%$$

Problem 33. 0.50 g of a mixture of K_2CO_3 and Li_2CO_3 requires 30 mL of a 0.25 N HCl solution for neutralization. What is the percentage composition of the mixture?

(Roorkee 1989)

Solution. Let the mass of K_2CO_3 in the mixture = x g

Mass of Li_2CO_3 in the mixture = $(0.50 - x)$ g



1 mole of K_2CO_3 reacts with 2 equivalents HCl

$$\begin{aligned} \therefore \text{Equivalent mass of } \text{K}_2\text{CO}_3 &= \frac{\text{Molecular mass of } \text{K}_2\text{CO}_3}{2} \\ &= \frac{2 \times 39 + 12 + 3 \times 16}{2} = \frac{138}{2} = 69 \text{ g/equiv.} \end{aligned}$$



1 mole of Li_2CO_3 reacts with 2 equivalents HCl

$$\begin{aligned} \text{Equivalent mass of } \text{Li}_2\text{CO}_3 &= \frac{\text{Molecular mass of } \text{Li}_2\text{CO}_3}{2} \\ &= \frac{2 \times 7 + 12 + 3 \times 16}{2} = \frac{74}{2} = 37 \text{ g/equiv.} \end{aligned}$$

$$\text{Gram-equivalents of } \text{K}_2\text{CO}_3 \text{ in 0.5 g mixture} = \frac{\text{Mass of } \text{K}_2\text{CO}_3}{\text{Equivalent mass of } \text{Li}_2\text{CO}_3} = \frac{x}{69}$$

$$\text{Gram-equivalent of } \text{Li}_2\text{CO}_3 \text{ in 0.5 g mixture} = \frac{\text{Mass of } \text{Li}_2\text{CO}_3}{\text{Equivalent mass } \text{Li}_2\text{CO}_3} = \frac{0.5 - x}{37}$$

Gram-equivalent of HCl in 30 mL of 0.25 N HCl = Normality \times V in litres

$$= 0.25 \text{ N} \times \frac{30}{1000} \text{ L} = 0.0075$$

1 gram-equivalent acid neutralizes 1 gram-equivalent base

$$\frac{x}{69} + \frac{0.5 - x}{37} = 0.0075$$

$$37x + 34.5 - 69x = 19.15$$

$$32x = 15.35$$

$$x = \frac{15.35}{32} = 0.48 \text{ g}$$

$$\% \text{K}_2\text{CO}_3 \text{ in the mixture} = \frac{0.48 \text{ g}}{0.50 \text{ g}} \times 100 \% = 96 \% \text{K}_2\text{CO}_3$$

$$\% \text{Li}_2\text{CO}_3 \text{ in the mixture} = 100\% - 96\% = 4\% \text{Li}_2\text{CO}_3$$

Problem 34. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate, sodium sulphate is gently heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 mL. A 1.5 g of the same sample requires 150 mL of (M/10) HCl for complete neutralization. Calculate the percentage composition of the components of the mixture.

(IIT/JEE 1992)

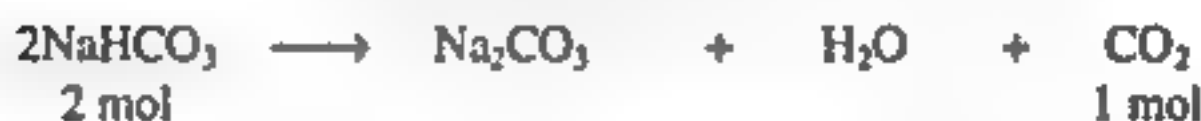
Solution. (a) Out of sodium carbonate, sodium bicarbonate and sodium sulphate, only sodium bicarbonate decomposes on heating to form carbon dioxide.

$$V_1 = 123.9 \text{ ml} \quad P_1 = 750 \text{ mm} \quad T_2 = 298 \text{ K}$$

$$PV = nRT$$

$$n = \text{Moles of } \text{CO}_2 = \frac{PV}{RT}$$

$$= \frac{(750/760) \text{ atm} \times (123.9/1000) \text{ L}}{0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.005 \text{ mol}$$



$$\therefore \text{Moles of NaHCO}_3 \text{ in the mixture} = 2 \times 0.005 \text{ mol} = 0.01 \text{ mol}$$

$$\text{Molecular mass of NaHCO}_3 = 23 + 1 + 12 + 48 = 84 \text{ g/mol}$$

$$\therefore \text{Mass of NaHCO}_3 \text{ in the mixture} = 0.01 \text{ mol} \times 84 \text{ g/mol} = 0.84 \text{ g}$$

$$\% \text{NaHCO}_3 \text{ in the mixture} = \frac{\text{Mass of NaHCO}_3}{\text{Mass of mixture}} \times 100$$

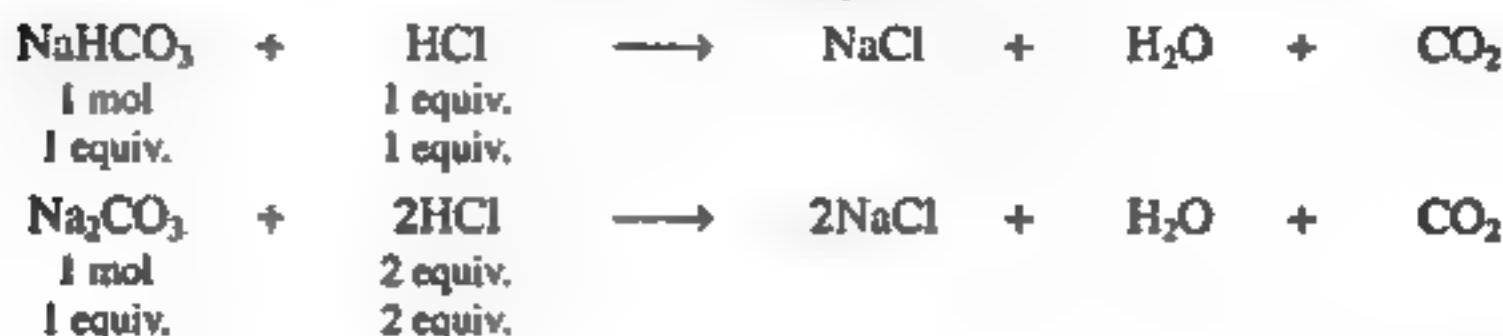
$$= \frac{0.84 \text{ g}}{2 \text{ g}} \times 100\% = 42\% \text{NaHCO}_3$$

$$1.5 \text{ g sample of the mixture requires } 150 \text{ mL of } \frac{\text{M}}{10} \text{ HCl}$$

$$= 150 \text{ mL} \times \frac{\text{M}}{10} = 15 \text{ M equiv. HCl}$$

$$2.0 \text{ g sample of the mixture requires} = \frac{15 \text{ M equiv.} \times 2.0 \text{ g}}{1.5 \text{ g}} = 20 \text{ M equiv. HCl}$$

$$= 0.02 \text{ equiv. HCl}$$



$$0.01 \text{ mol NaHCO}_3 = 0.01 \text{ equiv. NaHCO}_3$$

\therefore Equivalents of Na_2CO_3 in the mixture

$$= 0.02 \text{ equiv.} - 0.01 \text{ equiv.} = 0.01 \text{ equiv.}$$

$$\text{Molecular mass of Na}_2\text{CO}_3 = 2 \times 23 + 12 + 3 \times 16 = 126 \text{ g/mol}$$

$$\text{Equivalent mass of Na}_2\text{CO}_3 = \frac{\text{Molar mass}}{2} = \frac{126}{2} = 53 \text{ g/equiv}$$

$$\text{Amount of Na}_2\text{CO}_3 \text{ in the mixture} = \text{Normality} \times \text{Equivalent mass}$$

$$= 0.01 \text{ equiv.} \times 53 \text{ g/equiv.} = 0.53 \text{ g}$$

$$\% \text{ Na}_2\text{CO}_3 \text{ in the mixture} = \frac{0.53}{1} \times 100 = 26.5\% \text{ Na}_2\text{CO}_3$$

$$\% \text{ Na}_2\text{SO}_4 \text{ in the mixture} = 100\% - (42\% + 26.5\%) = 31.5\% \text{ Na}_2\text{SO}_4$$

Problem 35. A 1.2 g mixture of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 cm^3 of a solution, 20 cm^3 of this solution required 40 cm^3 of 0.1 N HCl for neutralization. Calculate the weight of Na_2CO_3 and K_2CO_3 in the mixture.

Solution. Let weight of $\text{Na}_2\text{CO}_3 = x \text{ g}$

$$\text{Weight of K}_2\text{CO}_3 = 1.2 - x \text{ g}$$

$$\text{Equivalent mass of Na}_2\text{CO}_3 = \frac{\text{Molecular mass}}{2} = \frac{106}{2} = 53 \text{ g/equiv.}$$

$$\text{Equivalent mass of K}_2\text{CO}_3 = \frac{\text{Molecular mass}}{2} = \frac{138}{2} = 69 \text{ g/equiv.}$$

$$\text{Gram-equivalents of Na}_2\text{CO}_3 \text{ in } 100 \text{ mL soln.} = \frac{x}{53}$$

$$\text{Gram-equivalents of K}_2\text{CO}_3 \text{ in } 100 \text{ mL soln.} = \frac{1.22 - x}{69}$$

$$\text{Total Gram-equivalents in } 100 \text{ mL soln.} = \frac{x}{53} + \frac{1.22 - x}{69}$$

$$\text{Total Gram-equivalents in } 20 \text{ mL soln.} = \left(\frac{x}{53} + \frac{1.22 - x}{69} \right) \times \frac{20}{100}$$

$$\text{Gram-equivalents of HCl in } 40 \text{ mL of } 0.1 \text{ N HCl} = 0.1 \text{ N} \times \frac{40}{1000} = 0.004 \text{ equivalent}$$

According to the law of normalities :

$$\left(\frac{x}{53} + \frac{1.2 - x}{69} \right) \times \frac{20}{100} = 0.004$$

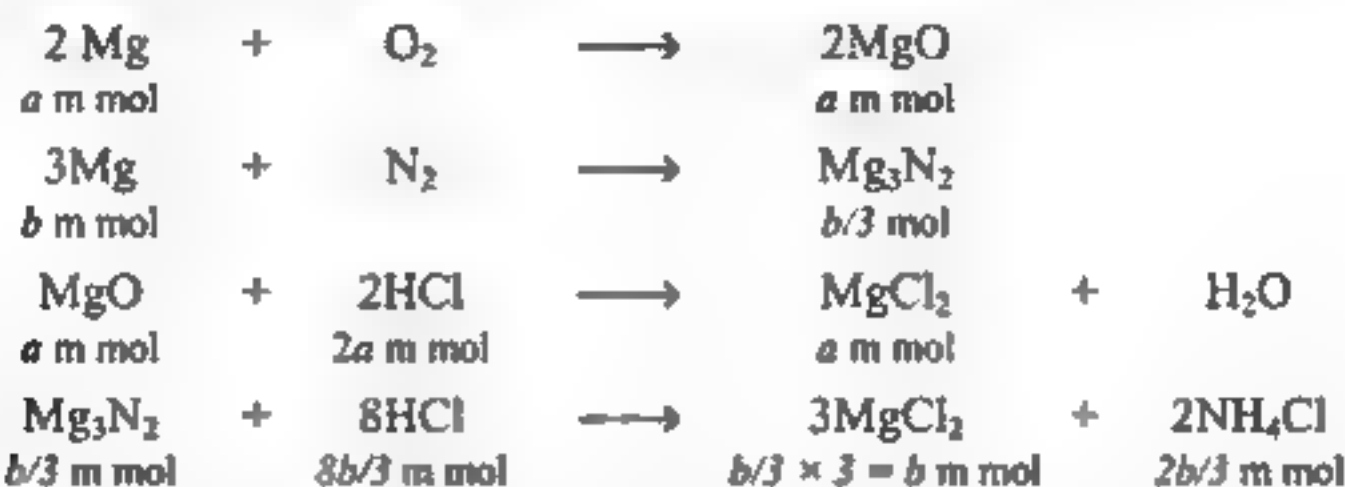
$$x = 0.5962 \text{ g}$$

$$\text{Weight of K}_2\text{CO}_3 = 1 - 0.5962 \text{ g} = 0.4038 \text{ g.}$$

Problem 36. A sample of magnesium was burnt in air to give a mixture of MgO and Mg_3N_2 . The ash was dissolved in 60 milli-equivalents of HCl and the resulting solution back titrated with NaOH . 12 milli-equivalents of NaOH were required to reach the end-point. An excess of NaOH was then added and the solution distilled. The ammonia

released was then trapped in 10 milli-equivalents of second acid solution. Back titration of this solution required 6 milli-equivalents of the base. Calculate the percentage of magnesium burnt to the nitride. (Roorkee 1998)

Solution. Let a millimoles of Mg reacts with oxygen to form MgO and b millimoles of Mg reacts with nitrogen to form Mg_3N_2 .



Moles of HCl required for dissolving MgO and $\text{Mg}_3\text{N}_2 = 2a \text{ m mol} + 8b/3 \text{ m mol}$

As HCl is a monobasic acid, 1 eq HCl = 1 mol HCl

Moles of HCl used for dissolving MgO + $\text{Mg}_3\text{N}_2 = 60 \text{ m mol} - 12 \text{ m mol} = 48 \text{ m mol}$

Moles of NH_4Cl formed = Moles of NH_3 liberated

= Moles of HCl used for absorbing NH_3

$$\frac{2b}{3} = 4$$

or

$$b = 6 \text{ m mol}$$

$$2a + \frac{8}{3} \times 6 = 48$$

$$2a = 48 - 16$$

$$a = 16 \text{ m mol}$$

$$\% \text{ Mg used for forming } \text{Mg}_3\text{N}_2 = \frac{6 \text{ m mol}}{(6 + 16) \text{ m mol}} \times 100 = 27.27\%$$

Problem 37. The formula weight of an acid is 82.0. In a titration, 100 cm^3 of solution of this acid containing 39.0 g of this acid per litre were completely neutralized by 95.0 cm^3 of aqueous NaOH containing 40 g of NaOH per litre. What is the basicity of this acid? (Roorkee 2000)

$$\text{Solution.} \quad \text{Equivalent mass of the acid} = \frac{\text{Molecular mass}}{\text{Basicity}}$$

$$\text{Normality of the acid} = \frac{\text{Gram-equiv.}}{\text{Volume of the solution}}$$

$$\text{Normality of acid} = \frac{\text{Mass}}{\text{Molecular mass}} \times \frac{\text{Basicity}}{V \text{ in litres}}$$

$$\text{Normality of NaOH} = \frac{40 \text{ g}}{40 \text{ g/equiv.}} = 1 \text{ N}$$

$$N_{\text{acid}} \times V_{\text{acid}} = N_{\text{NaOH}} \times V_{\text{NaOH}}$$

$$N_{\text{acid}} = \frac{N_{\text{NaOH}} \times V_{\text{NaOH}}}{V_{\text{acid}}} = \frac{1 \text{ N} \times 95/1000}{1 \text{ litre}} = 0.95 \text{ N}$$

$$\begin{aligned}\text{Basicity} &= \frac{N \times \text{Molecular mass} \times V \text{ in litre}}{\text{Mass of acid}} \\ &= \frac{0.95 \text{ N} \times 82 \text{ g/mol} \times 1 \text{ L}}{39 \text{ g}} = 2\end{aligned}$$

Problem 38. Gastric juice contains 3.0 g of HCl per litre. If a person produces 2.5 litre of gastric juice per day, how many antacid tablets each containing 400 mg of $\text{Al}(\text{OH})_3$ are needed to neutralize all the HCl produced in one day? (Dhanbad 1991)

Solution. Amount of HCl in 2.5 litres of Gastric juice

$$= 3 \times 2.5 = 7.5 \text{ g}$$



Mass of $\text{Al}(\text{OH})_3$ required for neutralizing 7.5 g HCl

$$= \frac{78 \text{ g}}{3 \times 36.5 \text{ g}} \times 7.5 \text{ g} = 5.342 \text{ g} = 5342 \text{ mg}$$

$$\text{No. of tablets of } \text{Al}(\text{OH})_3 \text{ needed} = \frac{5342 \text{ mg}}{400 \text{ mg}} = 13.35 \approx 14$$

Problem 39. A sample containing 0.4775 g of $(\text{NH}_4)_2 \text{C}_2\text{O}_4$ and inert materials was dissolved in water and made strongly alkaline with KOH, which converted NH_4^+ to NH_3 . The liberated ammonia was distilled into exactly 50.0 mL of 0.05035 M H_2SO_4 . The excess H_2SO_4 was back titrated with 11.3 mL of 0.1214 M NaOH. Calculate :

(a) Percent of N

(b) Percent of $(\text{NH}_4)_2 \text{C}_2\text{O}_4$

(Mol. wt. of $(\text{NH}_4)_2 \text{C}_2\text{O}_4 = 124.10$ and At. wt. of N = 14.0078) (MLNR 1994)

Solution.

Milli-equivalents of $(\text{NH}_4)_2 \text{C}_2\text{O}_4 = \text{Milli-equivalents of } \text{NH}_3 = \text{Milli-equivalents of N}$
 $= \text{Milli-equivalents of } \text{H}_2\text{SO}_4 \text{ used}$

$$\begin{aligned}\frac{W_{(\text{NH}_4)_2 \text{C}_2\text{O}_4}}{124.10/2} \times 1000 &= \text{Milli-equivalents of } \text{NH}_3 \\ &= (0.05035 \times 2 \times 50 - 11.3 \times 0.1214) = 3.663\end{aligned}$$

$$\therefore W_{(\text{NH}_4)_2 \text{C}_2\text{O}_4} = 0.2273$$

$$\begin{aligned}\therefore \text{Percentage of } (\text{NH}_4)_2 \text{C}_2\text{O}_4 &= \frac{\text{Mass of } (\text{NH}_4)_2 \text{C}_2\text{O}_4 \times 100}{\text{Mass of sample}} \\ &= \frac{0.2273}{0.4775} \times 100 = 47.8\%\end{aligned}$$

Also Milli-equivalents of N = Milli-equivalents of NH_3

$$\begin{aligned}\frac{w}{14} \times 1000 &= 3.663 \\ w_{\text{N}_2} &= 0.0513\end{aligned}$$

$$\therefore \text{Percentage of N} = \frac{0.0513}{0.4775} \times 100 = 10.74\%$$

Problem 40. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of KMnO_4 (20 mL) acidified with dilute H_2SO_4 . The same volume of the KMnO_4 solution is just decolourised by 10 mL of MnSO_4 in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2 . The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4 . Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2 .

Ans. (i) In acidic medium, MnO_4^- oxidises H_2O_2 to O_2 . The involved reactions are



(ii) In neutral medium, the reaction of MnO_4^- with Mn^{2+} are as follows.



(iii) The dissolution of MnO_2 in sodium oxalate in acidic medium involves the following reactions.



Amount of oxalate used in dissolving MnO_2 is

$$n_1 = V_1 M_1 = (10 \text{ mL}) (0.2 \text{ M}) \text{ m mol}$$

$$= (10 \text{ mL}) \left(\frac{0.2 \text{ mol}}{1000 \text{ mL}} \right) \text{ m mol} = 2 \times 10^{-3} \text{ mol}$$

From the reactions given above, we conclude that



$$\equiv \frac{1}{5} (2 \times 10^{-3} \text{ mol } \text{MnO}_4^-)$$

$$\equiv \frac{5}{2} \left[\frac{2}{5} (2 \times 10^{-3}) \text{ mol } \text{H}_2\text{O}_2 \right]$$

$$\equiv 2 \times 10^{-3} \text{ mol } \text{H}_2\text{O}_2$$

$2 \times 10^{-3} \text{ mol}$ of H_2O_2 is present in 20 mL of hydrogen peroxide solution. Hence, its molarity is

$$M = \frac{n}{V} = \frac{2 \times 10^{-3} \text{ mol}}{20 \times 10^{-3} \text{ L}} = 0.1 \text{ mol L}^{-1}.$$

PROBLEMS FOR PRACTICE

- What is the molarity of a solution made by dissolving 2 g perchloric acid (HClO_4) in enough water to make 200 mL of solution?
- How much KOH should be dissolved in 250 mL of the solution so that it is 0.4 N?
- How many moles are present in 300 mL of 0.03 M HNO_3 solution?
- How many millimoles are present in 250 mL of 0.25 M acetic acid, CH_3COOH ?
- How many milli-equivalents are present in 40 mL of 0.6 N oxalic acid?
- Calculate the normality of a 40 mL sample of H_2SO_4 containing 4.0 milli-equivalents of H_2SO_4 ?
- Calculate the normality of a 50 mL sample of formic acid containing 0.23 g of the acid?
- What is the equivalent mass of H_3BO_3 in the following titration? $\text{B} = 11$ amu.

$$\text{CH}^-(aq) + \text{H}_3\text{BO}_3(aq) \longrightarrow \text{H}_2\text{O} + \text{H}_2\text{BO}_3^-(aq)$$
- What is the equivalent-mass of H_3AsO_4 in the following titration? $\text{As} = 75$ amu.

$$\text{H}_3\text{AsO}_4(aq) + 2\text{OH}^-(aq) \longrightarrow \text{HAsO}_4^{2-}(aq) + 2\text{H}_2\text{O}$$
- What is the equivalent mass of $\text{Fe}(\text{OH})_2$ in the following reaction? $\text{Fe} = 56$ amu.

$$2\text{H}^+ + \text{Fe}(\text{OH})_2 \longrightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$$
- Sulphuric acid is a diprotic acid in water. What is the normality of 0.023 M H_2SO_4 as an acid?
- Barium hydroxide, $\text{Ba}(\text{OH})_2$, is a diacidic base in water. What is the molarity of 0.46 N $\text{Ba}(\text{OH})_2$ as a base?
- What is the final concentration of a solution made by mixing 50 mL of 0.5 M H_2SO_4 and 75 mL of 0.25 M H_2SO_4 ?
- How much water should be added to 50 mL of 3.5 M H_2SO_4 to make a solution that is 2.0 M H_2SO_4 ?
- Calculate the equivalent mass of H_2SO_4 in the following reaction:

$$\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$$
- 20 mL of $\text{Ba}(\text{OH})_2$ is neutralized completely by 15 mL of 0.05 M HNO_3 .
 (i) What is the molarity of $\text{Ba}(\text{OH})_2$?
 (ii) What is the normality of $\text{Ba}(\text{OH})_2$?
- How many millilitres of 0.06 N HCl is required to neutralize completely 12 mL of 0.05 N $\text{Ba}(\text{OH})_2$?
- 15 mL of H_3PO_4 solution is completely neutralized by 10 mL of 0.075 M H_2SO_4 . What is the concentration of H_3PO_4 solution?
- A solution was prepared by dissolving 6.3 g crystalline oxalic acid in one litre solution. 20 mL of this solution required 25 mL of 0.08 N NaOH for complete neutralization. What is the number of molecules of water of crystallization in a molecule of hydrated oxalic acid?
- In a titration in which two of the three protons of H_3PO_4 are neutralized, 30 mL of a phosphoric acid solution are titrated by 22 mL of 0.07 N NaOH.
 (a) What is the normality of phosphoric acid?
 (b) What is its molarity?

21. 3.155 g $\text{Ba(OH)}_2 \cdot x\text{H}_2\text{O}$ were dissolved in 1000 mL solution. 26.25 mL of this solution required 35 mL of 0.015 N H_2SO_4 for complete neutralization. What is the value of x ?
22. An impure sample (4.0 g) of NaOH containing K_2CO_3 as an impurity was dissolved in water to make 100 mL solution. 5 mL of this solution required 15 mL of 0.20 N HCl for complete neutralization. Calculate the percentage purity of NaOH.
23. 25 mL of 0.12 N acid solution requires 24 mL of the solution of a base for complete neutralization. The solution of the base contains 10.62 g/litre. Find the equivalent-mass of the base.
24. 22.5 mL HCl were required to exactly neutralize 25 mL of 0.1 N Na_2CO_3 solution. What is the normality of hydrochloric acid solution? How much water must be added to 200 mL of the acid solution to make it 0.1 N?
25. 1.0 g of a mixture of sodium chloride and anhydrous sodium carbonate is exactly neutralized by 50 mL of 0.5 N solution of acid. Calculate the percentage of NaCl in the mixture.
26. A solution contains 3.66×10^{22} HCl molecules in one litre of the solution. What is its normality?
27. Calculate the mass of zinc carbonate which would just neutralize 300 millilitres of 0.1 N sulphuric acid.
28. What will be the volume of a 3.0 percent solution of sodium carbonate necessary for neutralization of a litre of 0.1 N H_2SO_4 .
29. 1.5 g of an unknown acid H_nX neutralizes 40 mL of 0.25 N NaOH solution. What is the weight of one equivalent of the acid?
30. A certain amount of the mixture of K_2CO_3 and KHCO_3 was dissolved in 2 litres of water. 20 mL of the solution required 10 mL of 0.2 M HNO_3 for neutralization using phenolphthalein as the indicator. The same volume of the solution when titrated using methyl orange as the indicator required 25 mL of 0.2 M HNO_3 . Calculate the percent composition of the mixture.
31. A solution contains K_2CO_3 and KOH. 10 mL of the solution requires 5.0 mL of 0.2 N HCl for neutralization using phenolphthalein as the indicator. Methyl orange is then added when a further 13 mL of 0.1 N HCl was required. Calculate the concentration of K_2CO_3 and KOH in the solution.
32. 2.5 g of a mixture of BaCO_3 and CaCO_3 is dissolved in 50 mL of 1 N HNO_3 and the excess acid is neutralized by 0.4 g of solid NaOH.
 - (a) What is the percent composition of the mixture?
 - (b) What is the amount of NO_3^- ions in the solution?
33. 1.75 g of a mixture of $(\text{NH}_4)_2\text{SO}_4$ and NaCl were boiled with excess of sodium hydroxide solution and the ammonia gas evolved was passed into 120 mL of 0.2 N HCl. The resulting solution required 50 mL of a decinormal solution of nitric acid for complete neutralization. What is the percent composition of the mixture?
34. 75 mL of a saturated solution of lithium carbonate was decomposed completely by 42 mL of 0.025 M H_2SO_4 . What is the solubility of lithium carbonate? $L_1 = 7$ amu.
35. 20 g of a saturated magnesium carbonate solution required 16 mL of 0.04 N HNO_3 . What is the solubility of MgCO_3 ?

36. What volume of a solution of hydrochloric acid containing 73 g of acid per litre would suffice for the exact neutralization of sodium hydroxide obtained by allowing 0.46 g of metallic sodium to act upon water. (MLNR 1997)
37. A mixture of KOH and Na_2CO_3 solution required 15 mL of N/20 HCl using phenolphthalein as indicator. The same amount of alkali mixture when titrated using methyl orange as an indicator required 25 mL of same acid. Calculate the amounts of KOH and Na_2CO_3 present in solution. (BITS 1988)

ANSWERS

- | | | |
|---|--|-------------------|
| 1. 0.0995 M | 2. 5.6 g | 3. 0.009 moles |
| 4. 62.5 m moles | 5. 24 m equiv. | 6. 0.1 N |
| 7. 0.1 N | 8. 62 | 9. 71 |
| 10. 45 | 11. 0.046 N | 12. 0.23 M |
| 13. 0.35 M | 14. 37.5 mL | 15. 98 |
| 16. (i) 0.016 M | 17. 10 mL | 18. 9.8 g/litre |
| (ii) 70.038 N | | |
| 19. 2 | 20. (a) 0.51 N (b) 0.255 M | 21. 8 |
| 22. 95% | 23. 84.96 | 24. 22.2 mL |
| 25. 47% | 26. 0.06 N | 27. 1.881 g |
| 28. 176.7 mL | 29. 150 | |
| 30. $\text{K}_2\text{CO}_3 = 73.4\%$ | 31. $\text{K}_2\text{CO}_3 = 27.6 \text{ g/litre}$ | |
| $\text{KHCO}_3 = 26.6\%$ | $\text{KOH} = 3.36 \text{ g/litre}$ | |
| 32. (a) $\text{BaCO}_3 = 40\%$ $\text{CaCO}_3 = 60\%$ | (b) 3.1 g | |
| 33. $(\text{NH}_4)_2\text{SO}_4 = 71.7\%$ | 34. 1.036 g/litre | 35. 0.135 g/100 g |
| $\text{NaCl} = 28.3\%$ | | |
| 36. 10 mL | 37. $\text{KOH} = 0.014 \text{ g}$ | |
| | $\text{Na}_2\text{CO}_3 = 0.053 \text{ g}$ | |

Redox Reactions, Iodimetry and Iodometry

- Oxidizing agent.** It is a substance that
 - gives up oxygen or any electronegative element.
 - accepts hydrogen or any electropositive element.
 - accepts electrons.
- Reducing agent.** It is a substance that
 - gives up hydrogen or any electropositive element.
 - accepts oxygen or any electronegative element.
 - releases electrons.
- Redox reaction.** In a redox-reaction, electrons released by a reducing agent are absorbed by an oxidizing agent. A reaction is classified as a redox reaction if the oxidation states of the elements or groups of atoms change.
- Equivalent-mass of an oxidizing agent.** An equivalent of an oxidizing agent accepts 1 mole of electrons.

Equivalent mass of an oxidizing-agent

$$\begin{aligned}
 &= \frac{\text{Molecular mass of oxidizing agent}}{\text{Number of electrons gained per formula unit}} \\
 &= \frac{\text{Molecular mass}}{n}
 \end{aligned}$$

$$\therefore N = nM$$

Examples. (a) For the titration of potassium permanganate, KMnO_4 , against a reducing-agent, one MnO_4^- ion accepts five electrons. ($n = 5$)



$$\begin{aligned}
 \therefore \text{Equivalent mass of KMnO}_4 &= \frac{\text{Molecular mass of KMnO}_4}{5} \\
 &= \frac{158}{5} = 31.6 \text{ g/equiv.}
 \end{aligned}$$

$$N_{\text{KMnO}_4} = 5 M_{\text{KMnO}_4}$$

(b) For the reaction



$$\text{Equivalent mass of ClO}_3^- = \frac{\text{Molecular mass of ClO}_3^-}{6}$$

$$N_{\text{ClO}_3} = 6 M_{\text{ClO}_3}$$

(c) For the reaction :



$$\text{Equivalent mass of } I_2 = \frac{\text{Molecular mass of } I_2}{2}$$

$$N_{I_2} = 2 M_{I_2}$$

5. Equivalent mass of a reducing agent. One equivalent of a reducing agent gives up a mole of electrons and reduces one equivalent of an oxidizing agent.

Equivalent mass of reducing agent

$$= \frac{\text{Molecular mass}}{\text{Number of electrons released per formula unit}}$$

$$= \frac{\text{Molecular mass}}{n}$$

$$\therefore N = nM$$

Examples. (a) For the titration of sodium thiosulphate against iodine,



One electron is lost per $S_2O_3^{2-}$ formula unit, i.e. $n = 1$

$$\therefore \text{Equivalent mass of } Na_2S_2O_3 = \frac{\text{Molecular mass of } Na_2S_2O_3}{1}$$

$$N_{Na_2S_2O_3} = 1 M_{Na_2S_2O_3}$$

(b) For the titration of stannous chloride ($SnCl_2$) against an oxidizing agent



$$\text{Equivalent mass of } SnCl_2 = \frac{\text{Molecular mass of } SnCl_2}{2}$$

$$N_{SnCl_2} = 2 M_{SnCl_2}$$

(c) For the oxidation of NO_2^- in acidic medium



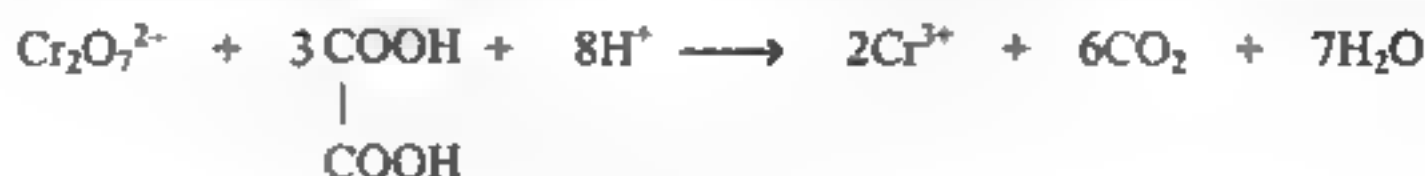
$$\text{Equivalent mass of } NO_2^- = \frac{\text{Molecular mass of } NO_2^-}{2}$$

$$N_{NO_2^-} = 2 M_{NO_2^-}$$

6. Oxidation number and equivalent mass.

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{\text{Total change in oxidation number of an element per formula unit}}$$

For the reaction between $K_2Cr_2O_7$ and oxalic acid in acid medium



$$\text{Change in oxidation number of } Cr^{3+} = 6 - 3 = 3$$

$$\text{Total change in oxidation number per formula unit } Cr_2O_7^{2-} = 2 \times 3 = 6$$

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{\text{Molecular mass of } K_2Cr_2O_7}{6}$$



Change in oxidation number of 1 C atom = $4 - 3 = 1$

Total change in oxidation number per formula unit, = $2 \times 1 = 2$

$$\text{Equivalent mass of } \begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} = \frac{\text{Molecular mass}}{2}$$

✓ SOLVED PROBLEMS

Problem 1. 0.79 g potassium permanganate crystals were dissolved in enough water and the solution diluted to 100 mL.

(a) What is the molarity of the solution ?

(b) What is the normality when KMnO_4 acts as an oxidizing agent in acidic medium?

Solution.

$$\begin{aligned} \text{Moles of KMnO}_4 &= \frac{\text{Mass of KMnO}_4}{\text{Molecular mass of KMnO}_4} \\ &= \frac{0.79 \text{ g}}{158 \text{ g mol}^{-1}} = 0.005 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Molarity of KMnO}_4 &= \frac{\text{Moles of KMnO}_4}{\text{Volume of solution in litres}} \\ &= \frac{0.005 \text{ moles}}{(100/1000) \text{ litre}} = 0.05 \text{ M} \end{aligned}$$



$$\text{Equivalent mass of KMnO}_4 = \frac{\text{Molecular mass of KMnO}_4}{5}$$

$$\begin{aligned} N_{\text{KMnO}_4} &= 5M_{\text{KMnO}_4} \\ &= 5 \times 0.05 = 0.25 \text{ N} \end{aligned}$$

Problem 2. What is the normality of 0.03 M sodium sulphite in the following reaction :



Solution.

$$\text{Equivalent mass of Na}_2\text{SO}_3 = \frac{\text{Molecular mass of Na}_2\text{SO}_3}{2}$$

$$N_{\text{Na}_2\text{SO}_3} = 2 M_{\text{Na}_2\text{SO}_3} = 2 \times 0.03 = 0.06 \text{ N}$$

Problem 3. Calculate the mass of CrCl_3 that should be dissolved in 250 mL solution to make it 0.1 N.



Solution.

$$\begin{aligned} \text{Equivalent mass of CrCl}_3 &= \frac{\text{Molecular mass of CrCl}_3}{3} \\ &= \frac{52 + 3 \times 35.5}{3} = \frac{158.5}{3} = 52.8 \text{ amu} \end{aligned}$$

$$\text{Equivalents of CrCl}_3 = N_{\text{CrCl}_3} \times V \text{ in litres}$$

$$= 0.1 \text{ N} \times \left(\frac{250}{1000} \right) \text{ litres} = 0.025$$

$$\begin{aligned} \text{Mass of CrCl}_3 &= \text{Equivalents CrCl}_3 \times \text{Equivalent-mass CrCl}_3 \\ &= 0.025 \text{ N} \times 52.8 = 1.32 \text{ g.} \end{aligned}$$

Problem 4. How many milli-equivalents are present in 45 mL of 0.07 N Hg_2Cl_2 ?

$$\begin{aligned} \text{Solution.} \quad \text{Milli-equivalents} &= \text{Normality} \times V \text{ in millilitres} \\ &= 0.07 \text{ N} \times 45 \text{ mL} = 3.15 \text{ milli-equivalents.} \end{aligned}$$

Problem 5. How many milli-equivalents are present in 450 millilitres of 0.024 M Na_2S solution when it acts as a reducing agent in the following reaction :



$$\begin{aligned} \text{Solution.} \quad \text{Equivalent-mass of Na}_2\text{S} &= \frac{\text{Molecular mass of Na}_2\text{S}}{8} \\ N_{\text{Na}_2\text{S}} &= 8 M_{\text{Na}_2\text{S}} = 8 \times 0.024 = 0.192 \text{ N} \\ \text{Milli-equivalents of Na}_2\text{S} &= N_{\text{Na}_2\text{S}} \times V \text{ in mL} \\ &= 0.192 \text{ N} \times 450 \text{ mL} = 86.4 \end{aligned}$$

Problem 6. 15 millilitres of 0.0045 N $\text{Na}_2\text{S}_2\text{O}_3$ solution reacts completely with 20 mL of an iodine solution according to the equation :



(a) What is the normality of I_2 solution ?

(b) What is its molarity ?

$$\begin{aligned} \text{Solution.} \quad N_1 V_1 &= N_2 V_2 \\ N_{\text{I}_2} &= \frac{N_{\text{Na}_2\text{S}_2\text{O}_3} \times V_{\text{Na}_2\text{S}_2\text{O}_3}}{V_{\text{I}_2}} \\ &= 0.0045 \text{ N} \times \frac{15 \text{ mL}}{20 \text{ mL}} = 0.0034 \text{ N} \\ \text{I}_2 + 2\text{e}^- &\longrightarrow 2\text{I}^- \\ \text{Equivalent mass of I}_2 &= \frac{\text{Molecular mass of I}_2}{2} \\ N_{\text{I}_2} &= 2 M_{\text{I}_2} \\ M_{\text{I}_2} &= \frac{N_{\text{I}_2}}{2} = \frac{0.0034}{2} = 0.0017 \text{ M.} \end{aligned}$$

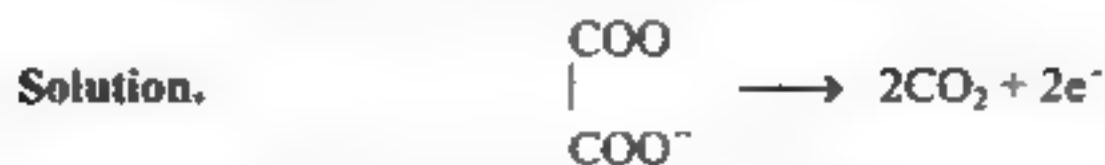
Problem 7. Exactly 40.0 mL of potassium permanganate solution react with 0.8 g of $\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the acidic medium according to the reaction :



(a) Calculate the normality of permanganate solution.

(b) Calculate its molarity.

(c) What is the strength of solution ?



$$\text{Equivalent mass of Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \frac{\text{Molecular mass of Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}}{2}$$

$$= \frac{170}{2} = 85 \text{ g/equiv.}$$

$$\text{Equivalents of Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \frac{\text{Mass in g}}{\text{Equivalent mass}} = \frac{0.8}{85}$$

According to the law of equivalents,

$$40 \text{ ml of } x \text{ N}_{\text{KMnO}_4} = \frac{0.8}{85}$$

$$\text{N}_{\text{KMnO}_4} = \frac{0.8}{85} \times \frac{1}{(40/1000)} \text{ litre} = 0.24 \text{ N}$$



$$\text{Equivalent mass of KMnO}_4 = \frac{\text{Molecular mass of KMnO}_4}{5}$$

$$= \frac{158}{5} = 31.6 \text{ g/equiv.}$$

$$\text{N}_{\text{KMnO}_4} = 5 \text{ M}_{\text{KMnO}_4}$$

$$\text{M}_{\text{KMnO}_4} = \frac{\text{N}_{\text{KMnO}_4}}{5} = \frac{0.24}{5} = 0.048 \text{ M}$$

$$\begin{aligned} \text{Strength of KMnO}_4 &= \text{N}_{\text{KMnO}_4} \times \text{Equivalent mass} \\ &= 0.24 \times 31.6 = 7.584 \text{ g/litre.} \end{aligned}$$

Problem 8. A 0.15 g sample of an unknown reducing agent is titrated with 35.5 ml of 0.05 N $\text{K}_2\text{Cr}_2\text{O}_7$. In the titration, the dichromate ion is reduced to Cr^{3+} . What is the equivalent mass of the reducing agent?

Solution. Milli-equivalents $\text{K}_2\text{Cr}_2\text{O}_7$ in

$$35.5 \text{ ml of } 0.05 \text{ N } \text{K}_2\text{Cr}_2\text{O}_7 = 0.05 \text{ N} \times 35.5 \text{ ml} = 1.775$$

$$\therefore \text{ Milli-equivalents of reducing of agent} = 1.775 \text{ milli-equivalents}$$

$$= \frac{1.775}{1000} = 0.001775 \text{ equivalents}$$

$$\text{Equivalent mass} = \frac{\text{Mass in g}}{\text{Equivalents}} = \frac{0.15}{0.001775} = 84.5 \text{ g/equiv.}$$

Problem 9. 5.5 g of a mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ requires 5.4 ml of 0.1 N KMnO_4 solution for complete oxidation. Calculate the gram-mole of hydrated ferric sulphate in the mixture.

(H = 1, O = 16, S = 32, Fe = 56)

(IIT/JEE 1979)

Solution.

$$\text{Molecular mass of FeSO}_4 \cdot 7\text{H}_2\text{O} = 56 + 32 + 64 + 7 \times 18 = 278 \text{ amu}$$

$$\text{Molecular mass of Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} = 2 \times 56 + 3(32 + 64) + 9 \times 18 = 562$$

Ferric sulphate does not react with KMnO_4 but ferrous sulphate is oxidized to ferric sulphate.



$$\text{Equivalent mass of FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{\text{Molecular mass}}{1} = \frac{278}{1} = 278 \text{ g/equiv.}$$

$$\begin{aligned} \text{Milli-equivalents of KMnO}_4 &= \text{Milli-equivalents FeSO}_4 \cdot 7\text{H}_2\text{O} \\ &= 0.1 \text{ N} \times 5.4 \text{ mL} = 0.54 \end{aligned}$$

$$\text{Equivalents of FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{0.54}{1000} = 0.54 \times 10^{-3} \text{ equivalents}$$

$$\begin{aligned} \text{Mass of FeSO}_4 \cdot 7\text{H}_2\text{O} &= \text{Equivalents} \times \text{Equivalent mass} \\ &= 0.54 \times 10^{-3} \times 278 = 0.15 \text{ g} \end{aligned}$$

$$\text{Mass of Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O in the mixture} = 5.5 - 0.15 = 5.35 \text{ g}$$

$$\begin{aligned} \text{Gram-mole of Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} &= \frac{\text{Mass in g}}{\text{Molecular mass}} \\ &= \frac{5.35 \text{ g}}{562 \text{ g/mol}} = 0.00952 \text{ mol.} \end{aligned}$$

Problem 10. Hydroxylamine reduces iron (III) according to the equation :



Iron (II) thus produced is estimated by titration with a standard permanganate solution. The reaction is



A 10 mL sample of hydroxylamine was diluted to 1 litre. 50 mL of this diluted solution was boiled with an excess of Iron (III) solution. The resulting solution required 12 mL of 0.02 M KMnO_4 solution for complete oxidation of Iron (II). Calculate the weight of hydroxylamine in one litre of the original solution. (IIT/JEE 1982)

$$\begin{aligned} \text{Solution.} \quad \text{Equivalent mass of KMnO}_4 &= \frac{\text{Molecular mass of KMnO}_4}{5} \\ N_{\text{KMnO}_4} &= 5 M_{\text{KMnO}_4} = 5 \times 0.02 = 0.1 \text{ N} \end{aligned}$$

$$\text{Milli-equivalents in 12 mL of 0.1 N KMnO}_4 = 0.1 \text{ N} \times 12 \text{ mL} = 1.2$$

\therefore According to the law of equivalents,

$$\begin{aligned} \text{Milli-equivalents of Fe}^{2+} &= 1.2 \text{ milli-equivalents} \\ &= 1.2 \times 10^{-3} \text{ equivalents} \end{aligned}$$

$$\text{Equivalent mass of Fe}^{2+} = \frac{\text{Molecular mass of Fe}^{2+}}{1}$$

$$\text{Moles of Fe}^{2+} \text{ produced} = 1.2 \times 10^{-3} \text{ moles}$$

$$\text{Molecular mass of NH}_2\text{OH} = 14 + 2 \times 1 + 16 + 1 = 33 \text{ amu}$$

From the balanced equation,

4 moles of Fe^{2+} are produced from $2 \times 33 \text{ g NH}_2\text{OH}$

$$1.2 \times 10^{-3} \text{ moles of Fe}^{2+} \text{ is produced from } \frac{2 \times 33 \times 1.2 \times 10^{-3}}{4} = 1.98 \times 10^{-2} \text{ g}$$

$$\text{Mass of NH}_2\text{OH in 1 litre solution} = \frac{1.98 \times 10^{-2} \times 1000}{50} \text{ g}$$

$$\text{Mass of NH}_2\text{OH in 1 litre original solution} = \frac{1.98 \times 10^{-2} \times 1000 \times 1000}{50 \times 10}$$

$$39.6 \text{ g NH}_2\text{OH.}$$

Problem 11. A 1.00 g sample of H_2O_2 solution containing $X\%$ H_2O_2 by weight requires X mL of a KMnO_4 solution for complete oxidation under acidic conditions. Calculate the normality of KMnO_4 solution. (IIT/JEE 1981)



$$\text{Equivalent mass of H}_2\text{O}_2 = \frac{\text{Molecular mass of H}_2\text{O}_2}{2} = \frac{34}{2} = 17 \text{ g/equiv.}$$

$$X \text{ mL of } N_{\text{KMnO}_4} = X \text{ mL of } N_{\text{H}_2\text{O}_2}$$

$$= \frac{x \times N}{1000} \text{ equivalents H}_2\text{O}_2 = \frac{x \times N \times 17}{1000} \text{ g H}_2\text{O}_2$$

Given:

100 g H_2O_2 solution contains x g H_2O_2

1 g H_2O_2 solution contains $\frac{x}{100}$ g H_2O_2

$$\therefore \frac{x}{100} = \frac{x \times N \times 17}{1000}$$

$$\text{or } N = \frac{1000}{100 \times 17} = 0.588 \text{ N KMnO}_4.$$

Problem 12. A sample of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ is strongly heated in air. The residue is Mn_3O_4 .

(a) The residue is dissolved in 100 ml of 0.1 N FeSO_4 containing dilute H_2SO_4 .

(b) The solution reacts completely with 50 mL of KMnO_4 solution.

(c) 25 mL of KMnO_4 solution used in step (b) requires 30 mL of 0.1 N FeSO_4 solution for the complete reaction.

Find the amount of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in the sample.

(Mn = 55, Fe = 56, S = 32)

(IIT/JEE 1980)

Solution. 25 mL of KMnO_4 solution = 30 mL of 0.1 N FeSO_4

$$50 \text{ mL of KMnO}_4 \text{ used} = 30 \times \frac{50}{25}$$

$$= 60 \text{ mL of 0.1 N FeSO}_4$$

$$\text{Volume of 0.1 N of FeSO}_4 = 100 \text{ mL}$$

$$\therefore \text{Volume of 0.1 N FeSO}_4 \text{ used in dissolving Mn}_3\text{O}_4 = 100 - 60 = 40 \text{ mL}$$



$$\text{Equivalent mass of Fe}^{2+} = \frac{\text{Molecular mass of Fe}^{2+}}{1}$$

$$\therefore 40 \text{ mL of 0.1 N FeSO}_4 = 40 \text{ mL of 0.1 M FeSO}_4$$

$$\text{Moles of FeSO}_4 = 0.1 \text{ M} \times \left(\frac{40}{1000} \right) \text{ litres} = 0.004 \text{ mol}$$



$$\text{Molecular mass of MnSO}_4 \cdot 4\text{H}_2\text{O} = 55 + 32 + 64 + 4 \times 18 = 223 \text{ amu}$$

$$\begin{aligned} 2 \text{ moles of FeSO}_4 \text{ gives } & 3 \text{ moles of MnSO}_4 \cdot 4\text{H}_2\text{O} \\ & = 3 \times 223 = 669 \text{ g} \end{aligned}$$

$$0.004 \text{ moles of FeSO}_4 \text{ gives } = \frac{669 \times 0.004}{2} = 1.338 \text{ g.}$$

Problem 13. A 0.5 g sample of an iron containing mineral, mainly in the form of CuFeS_2 , was reduced suitably to convert all the ferric iron into ferrous form and was obtained as a solution. In the absence of any interfering matter, the solution required 42 mL of 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution for titration. Calculate the percentage of CuFeS_2 in the mineral. (IIT/JEE 1976)

Solution.



$$\text{Equivalent mass of K}_2\text{Cr}_2\text{O}_7 = \frac{\text{Molecular mass of K}_2\text{Cr}_2\text{O}_7}{6}$$

$$\begin{aligned} N_{\text{K}_2\text{Cr}_2\text{O}_7} &= 6 M_{\text{K}_2\text{Cr}_2\text{O}_7} \\ &= 6 \times 0.01 = 0.06 \text{ N} \end{aligned}$$

$$\text{Milli-equivalents in 42 mL of 0.06 N K}_2\text{Cr}_2\text{O}_7 = 0.06 \text{ N} \times 42 \text{ mL} = 2.52$$

$$\therefore \text{Milli-equivalents of Fe}^{2+} \text{ in the solution} = 2.52$$

$$2.52 \text{ milli-equivalents} = \frac{2.52}{1000} = 0.00252 \text{ equivalents}$$



$$\therefore 1 \text{ equivalent of Fe}^{2+} = 1 \text{ mole Fe}^{2+} = 1 \text{ mole CuFeS}_2$$

$$0.00252 \text{ equivalents of Fe}^{2+} = 0.00252 \text{ moles CuFeS}_2$$

$$\text{Molecular mass of CuFeS}_2 = 63.5 + 55.8 + 2 \times 32 = 183.3 \text{ amu}$$

$$\text{Mass of CuFeS}_2 \text{ in the sample} = 0.00252 \times 183.3 = 0.4619 \text{ g.}$$

$$\text{Percentage of CuFeS}_2 = \frac{0.4619 \text{ g} \times 100}{0.5 \text{ g}} = 92.38\%.$$

Problem 14. 1.000 g of a moist sample of a mixture of potassium chloride and potassium chlorate was dissolved in water and made upto 250 mL. 25 mL of this solution was treated with SO_2 to reduce the chlorate to chloride and excess SO_2 was removed by boiling. The total chloride was precipitated as silver chloride. The weight of the precipitate was 0.1435 g. In another experiment, 25 mL of the original solution was heated with 30 mL of 0.2 N ferrous sulphate solution and unreacted ferrous sulphate required 37.5 mL of 0.08 N solution of an oxidizing agent for complete oxidation. Calculate the molar ratio of the chlorate to the chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to the equation :



Solution. Milli-equivalents in 37.5 mL of 0.08 N oxidizing agent

$$= 0.08 \text{ N} \times 37.5 \text{ mL} = 3$$

∴ Milli-equivalents of FeSO_4 unreacted = 3

Milli-equivalents in 30 mL of 0.20 N FeSO_4 = $0.02 \text{ N} \times 30 \text{ mL} = 6$

Milli-equivalents of FeSO_4 reacted = Milli-equivalents of KClO_3
 $= 6 - 3 = 3$

As 1 mole ClO_3^- reacts with 6 moles Fe^{2+}

∴ Milli-moles of KClO_3 = $\frac{3}{6} = 0.5 \text{ millimoles} = 0.5 \times 10^{-3} \text{ mol.}$

Molecular mass AgCl = $108 + 35.5 = 143.5 \text{ amu}$

25 ml of the solution = 0.1435 g AgCl

= $\frac{0.1435}{143.5} = 1 \times 10^{-3} \text{ mol AgCl}$

$\text{ClO}_3^- \rightleftharpoons \text{Cl}^-$

$0.5 \times 10^{-3} \text{ moles ClO}_3^- = 0.5 \times 10^{-3} \text{ moles of Cl}$

∴ Moles of KCl = $1 \times 10^{-3} - 0.5 \times 10^{-3} = 0.5 \times 10^{-3}$

$\text{KClO}_3 : \text{KCl} = 0.5 \times 10^{-3} : 0.5 \times 10^{-3} = 1 : 1.$

They are present in equimolar proportions.

Problem 15. 4.0 g sample of bleaching powder were suspended in 500 mL water. 25 mL of this suspension was treated with excess KI and HCl and the iodine so liberated required 15 mL of a decinormal $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete reduction. What is the percentage of available chlorine in the bleaching powder?

Solution.



1 mole CaOCl_2 = 1 mole Cl_2 = 1 mole I_2

Milli-equivalents in 15 mL of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ = $0.1 \text{ N} \times 15 \text{ mL} = 1.5$

∴ Milli-equivalents of I_2 = Milli-equivalents of Cl_2 = 1.5
 $= 1.5 \times 10^{-3} \text{ equivalents}$



Equivalent mass of Cl_2 = $\frac{\text{Molecular mass of Cl}_2}{2}$

= $\frac{71}{2} = 35.5 \text{ g/equiv.}$

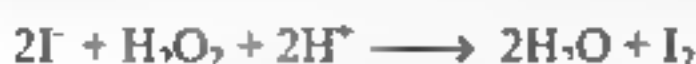
Mass of Cl_2 in 25 mL suspension = $\frac{1.5}{1000} \times 35.5 \text{ g}$

Mass of Cl_2 in 500 mL suspension = $\frac{1.5 \times 35.5 \times 500}{1000 \times 25} = 1.065 \text{ g}$

Percentage of available chlorine = $\frac{1.065 \text{ g}}{4.0 \text{ g}} \times 100 = 26.6\%.$

Problem 16. An excess of acidified solution of potassium iodide was added to 20 millilitres of hydrogen peroxide solution and the iodine so liberated required 15 mL of

0.4 N sodium thiosulphate solution for iodometric titration. Calculate the volume strength of H_2O_2 solution.



$$\text{Milli-equivalents in 15 mL of 0.4 N } \text{Na}_2\text{S}_2\text{O}_3 = 0.4 \text{ N} \times 15 \text{ mL} = 6.0$$

$$\text{Milli-equivalents of } \text{I}_2 = \text{Milli-equivalents of } \text{H}_2\text{O}_2$$

$$= 6.0 \text{ Milli-equivalents}$$

$$= 6.0 \times 10^{-3} \text{ equivalents}$$

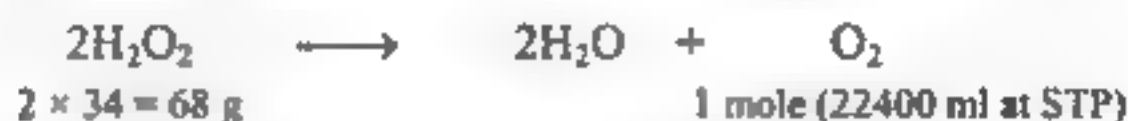


$$\text{Equivalent mass of } \text{H}_2\text{O}_2 = \frac{\text{Molecular mass of } \text{H}_2\text{O}_2}{2}$$

$$= \frac{34}{2} = 17 \text{ g/equiv.}$$

$$\text{Mass of } \text{H}_2\text{O}_2 \text{ in 20 mL solution} = 6.0 \times 10^{-3} \times 17 \text{ g}$$

$$\text{Mass of } \text{H}_2\text{O}_2 \text{ in 1 mL solution} = \frac{6.0 \times 10^{-3} \times 17 \times 1}{20} = 0.0051 \text{ g}$$



$$\text{Volume strength of } \text{H}_2\text{O}_2 = \text{Volume of oxygen (mL) liberated at STP from 1 mL of } \text{H}_2\text{O}_2 \text{ solution}$$

$$= \frac{22400 \text{ mL}}{68 \text{ g}} \times 0.0051 \text{ g} = 1.68 \text{ mL.}$$

Problem 17. 0.4 g sample of a copper ore was converted into copper sulphate solution. The resulting solution was acidified with dilute acetic acid and excess KI added. The liberated iodine required 0.248 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ for complete reaction. What is the percentage of copper in the ore?



$$\begin{aligned} \text{Equivalent mass of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} &= \frac{\text{Molecular mass of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}}{1} \\ &= 248 \text{ g/equiv} \end{aligned}$$



$$\text{Equivalent mass of } \text{Cu}^{2+} = \frac{\text{Molecular mass of } \text{Cu}^{2+}}{1} = 63.5 \text{ g/equiv}$$

$$0.248 \text{ g } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = \frac{0.248 \text{ g}}{248 \text{ g}} = 0.001 \text{ equivalents}$$

$$0.001 \text{ equivalents of } \text{S}_2\text{O}_3^{2-} = 0.001 \text{ equiv. } \text{I}_2 = 0.001 \text{ equiv } \text{Cu}^{2+}$$

$$\text{Mass of Cu} = 0.001 \times 63.5 = 0.0635 \text{ g Cu}$$

$$\text{Percentage of Cu in the ore} = \frac{0.0635 \text{ g}}{0.4 \text{ g}} \times 100 = 15.88\% \text{ Cu.}$$

Problem 18. (a) CuSO_4 reacts quantitatively with KI in an acidic medium to liberate I_2 . Write a balanced equation for this reaction.

(b) Mercuric iodate, $\text{Hg}_5(\text{IO}_6)_2$ reacts with a mixture of KI and HCl according to the following equation :



The liberated iodine is treated with $\text{Na}_2\text{S}_2\text{O}_3$ solution, one mL of which is equivalent to 0.0499 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. What volume in mL of $\text{Na}_2\text{S}_2\text{O}_3$ will be required to react with iodine liberated from 0.7245 g of $\text{Hg}_5(\text{IO}_6)_2$?

(Hg = 200.5 ; Cu = 63.5 ; I = 127)

(IIT/JEE 1970)



$$\text{Molecular mass of } \text{Hg}_5(\text{IO}_6)_2 = 5 \times 200.5 + 2 [127 + 6 \times 16] = 1448.5 \text{ amu}$$

$$\text{Molecular mass of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 249.5 \text{ amu}$$

From the given equation :

$$1 \text{ mole } \text{Hg}_5(\text{IO}_6)_2 = 8 \text{ moles } \text{I}_2$$

$$1448.5 \text{ g } \text{Hg}_5(\text{IO}_6)_2 = 8 \text{ moles } \text{I}_2$$

$$0.7245 \text{ g } \text{Hg}_5(\text{IO}_6)_2 = \frac{8 \times 0.7245}{1448.5} \text{ mol } \text{I}_2$$



$$1 \text{ mole } \text{I}_2 = 2 \text{ moles } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$$

$$\frac{8 \times 0.7245}{1448.5} \text{ moles } \text{I}_2 = \frac{2 \times 8 \times 0.7245}{1448.5} \text{ moles } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$$

$$= \frac{2 \times 8 \times 0.7245}{1448.5} \times 249.5 \text{ g } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$$

Given: $0.0499 \text{ g } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 1 \text{ ml } \text{Na}_2\text{S}_2\text{O}_3$

$$\text{Volume of } \text{Na}_2\text{S}_2\text{O}_3 \text{ required} = \frac{2 \times 8 \times 0.7245 \times 249.5}{1448.5 \times 0.0499} = 40 \text{ mL } \text{Na}_2\text{S}_2\text{O}_3$$

Problem 19. A 0.6 g of sample of pyrolusite was dissolved in a solution containing 5 mL of 6 N H_2SO_4 and 0.9 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (oxalic acid crystals). The excess oxalate required 24.00 millilitres of KMnO_4 solution for titration. Each millilitre of KMnO_4 solution oxidizes the iron (II) in 0.03058 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Calculate the percent MnO_2 in the sample.



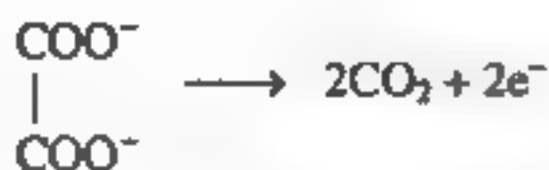
$$1 \text{ mole } \text{MnO}_2 = 1 \text{ mole } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$$

$$87 \text{ g } \text{MnO}_2 = 126 \text{ g } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$$

$$\text{Molecular mass of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278 \text{ amu}$$

Given : $1 \text{ mL } \text{KMnO}_4 = 0.03058 \text{ g } \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

$$= \frac{0.03058}{278} \text{ equivalent } \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$$



$$\text{Equivalent-mass of H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \frac{\text{Molecular mass}}{2} = \frac{126}{2} = 63 \text{ g/equiv.}$$

$$24 \text{ mL KMnO}_4 = \frac{24 \times 0.03058}{278} \text{ equivalents H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$$

$$= \frac{24 \times 0.03058}{278} \times 63$$

$$= 0.1663 \text{ g H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$$

\therefore Mass of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ that reacted with MnO_2 in pyrolusite

$$= 0.9 - 0.1663 = 0.7337 \text{ g}$$

$$126 \text{ g H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 87 \text{ g MnO}_2$$

$$0.7337 \text{ g H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \frac{87 \times 0.7337}{126} \text{ g MnO}_2$$

$$\therefore \text{Percent MnO}_2 = \frac{87 \times 0.7337}{126 \times 0.6} \times 100 = 84.4\% \text{ MnO}_2$$

Problem 20. 0.5 g sample of limonite containing iron as Fe_2O_3 is reduced to iron (II) in solution and titrated with 35.15 mL of a potassium dichromate solution. The oxidizing power of 15 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution is equivalent to 25 millilitres of KMnO_4 solution. The iron value of KMnO_4 solution is 0.00475 g. What is the percentage of Fe_2O_3 in the sample of limonite? $\text{Fe} = 56 \text{ amu}$.

$$\text{Solution,} \quad 1 \text{ mL KMnO}_4 = 0.00475 \text{ g Fe} = \frac{0.00475}{56} \text{ equivalent}$$

$$N_{\text{KMnO}_4} = \frac{0.00475 \times 1000}{56}$$

$$N_{\text{K}_2\text{Cr}_2\text{O}_7} = \frac{0.00475 \times 1000}{56} \times \frac{25}{15} = 0.14 \text{ N}$$

$$N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7} = \text{equivalents Fe}$$

$$0.14 \text{ N} \times \left(\frac{35.15}{1000} \right) \text{ litres} = \text{equivalents Fe}$$

$$\text{g - Fe} = \frac{0.14 \times 35.15 \times 56}{1000} \text{ g Fe}$$



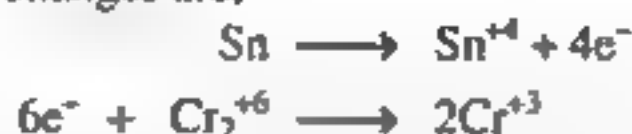
$$2 \times 56 \text{ g Fe} = 160 \text{ g Fe}_2\text{O}_3$$

$$\text{Mass of Fe}_2\text{O}_3 = \frac{0.14 \times 35.15 \times 56}{1000} \times \frac{160}{2 \times 56}$$

$$\begin{aligned} \text{Percentage of Fe}_2\text{O}_3 &= \frac{0.14 \times 35.15 \times 56}{1000} \times \frac{160 \times 100}{2 \times 56 \times 0.5} \\ &= 78.7\% \text{ Fe}_2\text{O}_3 \end{aligned}$$

Problem 21. Metallic tin in the presence of HCl is oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ to stannic chloride. What volume of decinormal dichromate solution would be reduced by 1 g of tin? (MLNR 1994)

Solution. The redox changes are,



\therefore Milli-equivalents of Sn = Milli-equivalents of $\text{K}_2\text{Cr}_2\text{O}_7$

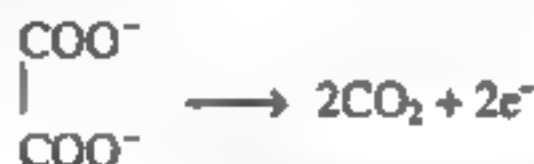
$$\begin{aligned}\text{Milli-equivalents of Sn in 1 g} &= \frac{\text{Mass of tin}}{\text{Eq. mass of tin}} \times 1000 \\ &= \frac{\text{Mass of tin}}{\text{At. mass of tin} / 4} \times 1000 = \frac{1\text{g}}{(118.7/4)} \times 1000\end{aligned}$$

$$\text{Milli-equivalents of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{N}{10} \times V$$

$$\therefore \frac{1}{(118.7/4)} \times 1000 = \frac{N}{10} \times V$$

or $V = 336.98 \text{ mL.}$

Problem 22. Find out the % of oxalate ion in given sample of oxalate salt of which 0.3 g dissolved in 100 mL of water required 90 mL of N/20 KMnO_4 for complete oxidation. (IIT/JEE 1979)



$$\begin{aligned}\text{Equivalent mass of oxalate ion} &= \frac{\text{Molecular mass of oxalate ion}}{2} \\ &= \frac{88}{2} = 44 \text{ g/equiv.}\end{aligned}$$

Milli-equivalents of oxalate ion = Milli-equivalents of KMnO_4

$$\frac{W}{E} \times 1000 = \frac{N}{20} \times 90 \text{ mL}$$

$$\frac{W}{44} \times 1000 = \frac{N}{20} \times 90 \text{ mL}$$

or $W = \frac{1}{20} \times 90 \times \frac{44}{1000} = 0.198 \text{ g}$

$$\begin{aligned}\% \text{ Purity} &= \frac{\text{Mass of oxalate in the sample}}{\text{Mass of sample}} \times 100 \\ &= \frac{0.198 \text{ g}}{0.3 \text{ g}} \times 100 = 66\%.\end{aligned}$$

Problem 23. 50 mL of an aqueous solution of H_2O_2 was treated with an excess of KI solution in dil. H_2SO_4 , the liberated iodine required 20 mL of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete reaction. Calculate concentration of H_2O_2 in g/litre. (Roorkee 1981)

Solution. Milli-equivalent of H_2O_2 = Milli-equivalent of KI
 = Milli-equivalent of I_2 liberated
 = Milli-equivalent of $\text{Na}_2\text{S}_2\text{O}_3$ used

Milli-equivalent of H_2O_2 = Milli-equivalent of $\text{Na}_2\text{S}_2\text{O}_3$ used

$$N_{\text{H}_2\text{O}_2} \times 50 \text{ mL} = 0.1 \text{ N} \times 20 \text{ mL}$$

or

$$N_{\text{H}_2\text{O}_2} = \frac{0.1 \times 20}{50} = 0.04 \text{ N}$$



$$\text{Equivalent mass of } \text{H}_2\text{O}_2 = \frac{\text{Molecular mass}}{2} = \frac{34}{2} = 17 \text{ g/equiv.}$$

$$\begin{aligned} \text{Strength of } \text{H}_2\text{O}_2 &= \text{N} \times \text{Equivalent-mass} \\ &= 0.04 \text{ N} \times 17 \text{ g/equiv.} = 0.68 \text{ gL}^{-1} \end{aligned}$$

Problem 24. A solution of 0.1 M KMnO_4 is used for the reaction :



What volume of solution in mL will be required to react with 0.158 g of $\text{Na}_2\text{S}_2\text{O}_3$?
 (MLNR 1991)

Solution. $\text{S}_2\text{O}_3^{2-} + 5\text{H}_2\text{O} \longrightarrow 2\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^-$

$$\begin{aligned} \text{Equivalent mass of } \text{Na}_2\text{S}_2\text{O}_3 &= \frac{\text{Molecular mass}}{\text{No. of electrons lost per molecule}} \\ &= \frac{158}{8} \end{aligned}$$



$$\begin{aligned} \text{Equivalent mass of } \text{KMnO}_4 &= \frac{\text{Molecular mass of } \text{KMnO}_4}{\text{No. of electrons gained per molecule}} \\ &= \frac{\text{Molecular mass}}{6/2} = \frac{\text{Molecular mass}}{3} \end{aligned}$$

$$\text{N} = n\text{M}$$

$$N_{\text{KMnO}_4} = 3 \times 0.1 \text{ M} = 0.3 \text{ N}$$

Milli-equivalent of KMnO_4 = Milli-equivalent of $\text{Na}_2\text{S}_2\text{O}_3$

$$0.3 \text{ N} \times V = \frac{0.158 \text{ g}}{158/8} \times 1000$$

or

$$V = \frac{0.158}{158} \times \frac{8}{0.3} \times 1000 = 26.67 \text{ mL.}$$

Problem 25. 25 g of a sample of FeSO_4 was dissolved in water containing dil. H_2SO_4 and the volume made upto 1 litre. 25 mL of this solution required 20 mL of N/10 KMnO_4 for complete oxidation. Calculate % of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in given sample.

(Roorkee 1982)

Solution. Milli-equivalent of FeSO_4 in 25 mL = Milli-equivalent of KMnO_4

$$N_{\text{FeSO}_4} \times 25 \text{ mL} = \frac{\text{N}}{10} \times 20 \text{ mL}$$

$$N_{\text{FeSO}_4} = \frac{1}{10} \times \frac{20}{25} = \frac{2}{25} N$$

$$\text{Mass of FeSO}_4 \text{ in 1L solution} = N \times \text{Equivalent mass}$$

$$= \frac{2}{25} \times \frac{278}{1} = 22.24 \text{ g}$$

$$\% \text{ of FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{\text{Mass of FeSO}_4 \cdot 7\text{H}_2\text{O}}{\text{Mass of sample}} \times 100$$

$$= \frac{22.24 \text{ g}}{25 \text{ g}} \times 100 = 88.96\%.$$

Problem 26. 25 mL of a solution containing Fe^{2+} and Fe^{3+} sulphate acidified with H_2SO_4 is reduced by 3 g of metallic zinc. The solution required 34.25 mL of $N/10$ solution of $\text{K}_2\text{Cr}_2\text{O}_7$ for oxidation. Before reduction with zinc, 25 mL of the same solution required 22.45 mL of same $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Calculate the strength of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ in solution. (IIT/JEE 1979)

Solution. (i) Milli-equiv. of $\text{FeSO}_4 = \text{Milli-equiv. of } \text{K}_2\text{Cr}_2\text{O}_7$

$$N_{\text{FeSO}_4} \times 25 \text{ mL} = \frac{N}{10} \times 22.45$$

$$N_{\text{FeSO}_4} = \frac{N}{10} \times \frac{22.45}{25}$$

$$\text{Strength of FeSO}_4 \text{ in solution} = N \times \text{Equivalent mass}$$

$$= \frac{1}{10} \times \frac{22.45}{25} \times 152 = 1.36 \text{ g/L}$$

(ii) Zinc reduces Fe^{3+} to Fe^{2+} .

Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ solution used for oxidation of Fe^{2+} (obtained by reduction with zinc)
 $= 34.25 - 22.45 = 11.80 \text{ mL}$

$$\text{Milli-equiv. of Fe}^{2+} = \text{Milli-equiv. of Fe}^{3+}$$

$$= \text{Milli-equiv. of } \text{K}_2\text{Cr}_2\text{O}_7 \cdot 2\text{FeSO}_4 = 1 \text{ Fe}_2(\text{SO}_4)_3$$

$$\text{Milli-equiv. of (Fe}^{2+} = \text{Fe}^{3+}) \times 25 = \frac{N}{10} \times 11.80$$

$$\text{Milli-equiv. of Fe}_2(\text{SO}_4)_3 = \frac{N}{10} \times \frac{11.80}{25}$$

$$\text{Strength of Fe}_2(\text{SO}_4)_3 \text{ in solution} = \frac{N}{10} \times \frac{11.80}{25} \times \frac{\text{Mol. mass of Fe}_2(\text{SO}_4)_3}{2}$$

$$= \frac{1}{10} \times \frac{11.80}{25} \times \frac{400}{2} = 9.45 \text{ g/L.}$$

Problem 27. A 0.804 gm sample of iron ore was dissolved in acid. Iron was reduced to +2 state and it required 47.2 mL of 0.112 N KMnO_4 solution for titration. Calculate the percentage of Fe and Fe_3O_4 in the ore. (Roorkee 1988)

Solution. Equivalents of KMnO_4 used $= N_{\text{KMnO}_4} \times V_{\text{KMnO}_4}$ in litre

$$= 0.112 N \times \frac{47.2}{1000} \text{ litre} = 0.005286 \text{ equiv.}$$

According to the law of equivalents,

$$\begin{aligned}\text{Equivalents of Fe}^{2+} \text{ in solution} &= 0.005286 \text{ equiv.} \\ &= 0.005286 \times 55.85 \text{ g Fe} = 0.2952 \text{ g Fe}\end{aligned}$$

$$\text{Molecular mass of Fe}_3\text{O}_4 = 3 \times 55.85 + 4 \times 16 = 231.55 \text{ g/mol}$$

$$\begin{array}{ccc} 3\text{Fe} & = & \text{Fe}_3\text{O}_4 \\ 3 \times 55.85 \text{ g} & & 231.55 \text{ g} \end{array}$$

$$\text{Mass of Fe}_3\text{O}_4 = \frac{231.55 \text{ g} \times 0.2952 \text{ g}}{3 \times 55.85 \text{ g}} = 0.4080 \text{ g}$$

$$\begin{aligned}\text{Mass \% of Fe} &= \frac{\text{Mass of Fe}}{\text{Mass of ore}} \times 100\% \\ &= \frac{0.2952 \text{ g}}{0.804 \text{ g}} \times 100 = 36.7\% \text{ Fe}\end{aligned}$$

$$\text{Mass \% of Fe}_3\text{O}_4 = \frac{0.4080 \text{ g}}{0.804 \text{ g}} \times 100 = 50.8\% \text{ Fe}_3\text{O}_4.$$

Problem 28. The label on a bottle of hydrogen peroxide solution reads as 10 volumes. Report the concentration of hydrogen peroxide in percentage. (Roorkee 1989)

Solution. 10 volume H_2O_2 solution means that 10 litres of oxygen is obtained at STP by decomposition of 1 litre H_2O_2 solution.



22.4 L oxygen is obtained from 68 g H_2O_2

$$\therefore 10 \text{ L oxygen is obtained from } \frac{68 \text{ g}}{22.4 \text{ L}} \times 10 \text{ L} = 30.35 \text{ g H}_2\text{O}_2$$

\therefore 1000 cm^3 of H_2O_2 solution contains 30.35 g H_2O_2

$$100 \text{ cm}^3 (\approx 100 \text{ g}) \text{ H}_2\text{O}_2 \text{ solution contains } \frac{30.35 \text{ g}}{1000 \text{ cm}^3} \times 100 \text{ cm}^3 = 3.035 \text{ g H}_2\text{O}_2$$

$$\text{Strength of 10 volume H}_2\text{O}_2 = 3.035\%.$$

Problem 29. 5.0 g of bleaching powder was suspended in water and volume made up to half a litre. 20 mL of this suspension when acidified with acetic acid and treated with excess of potassium iodide solution liberated iodine which required 20 mL of a decinormal hypo solution for titration. Calculate the percentage of available chlorine in the bleaching powder. (Roorkee 1990)



$$1 \text{ mole CaOCl}_2 \equiv 1 \text{ mole Cl}_2 \equiv 1 \text{ mole I}_2$$

$$\text{Milli-equivalents in 20 mL of 0.1 N Na}_2\text{S}_2\text{O}_3 = 0.1 \text{ N} \times 20 \text{ mL} = 2.0 \text{ m. equiv.}$$

$$\begin{aligned}\text{Milli-equivalents of I}_2 &= \text{Milli-equivalents of Cl}_2 \\ &= 2.0 \text{ Milli-equivalents} \\ &= 2.0 \times 10^{-3} \text{ equivalents}\end{aligned}$$



$$\text{Equivalent mass of Cl}_2 = \frac{\text{Molecular mass of Cl}_2}{2} = \frac{71}{2} = 35.5 \text{ g/equiv.}$$

$$\text{Mass of Cl}_2 \text{ in 20 mL suspension} = \frac{2.0}{1000} \times 35.5 \text{ g}$$

$$\text{Mass of Cl}_2 \text{ in 500 mL suspension} = \frac{2.0 \times 35.5 \times 500}{1000 \times 20} = 1.775 \text{ g}$$

$$\text{Percentage of available chlorine} = \frac{1.775 \text{ g}}{5.0 \text{ g}} \times 100\% = 35.5\%.$$

Problem 30. (a) (i) What is the weight of sodium bromate and molarity of solution necessary to prepare 85.5 mL of 0.672 N solution when the half-cell reaction is



(ii) What would be the weight as well as molarity if the half-cell reaction is



Solution. (a) Molecular mass of $\text{NaBrO}_3 = 23 + 80 + 3 \times 16 = 151 \text{ g/mol}$

$$\text{Equivalent mass of NaBrO}_3 = \frac{\text{Molecular mass of NaBrO}_3}{6}$$

$$N_{\text{NaBrO}_3} = 6 M_{\text{NaBrO}_3}$$

$$N_{\text{NaBrO}_3} = \frac{N_{\text{NaBrO}_3}}{6} = \frac{0.672}{6} = 0.112 \text{ M.}$$

$$\begin{aligned} \text{Moles NaBrO}_3 \text{ in 85.5 mL of 0.112 M solution} &= \text{Molarity} \times \text{Volume in litres} \\ &= 0.112 \text{ M} \times (85.5/1000 \text{ litres}) \\ &= 0.009576 \text{ mol.} \end{aligned}$$

$$\begin{aligned} \text{Weight of NaBrO}_3 \text{ required} &= \text{Moles} \times \text{Molecular mass} \\ &= 0.009576 \text{ mol} \times 151 \text{ g/mol} \\ &= 1.446 \text{ g.} \end{aligned}$$

(ii) Number of electrons accepted per molecule is $\frac{10}{2} = 5$ in the following reaction :



$$\text{Equivalent mass of NaBrO}_3 = \frac{\text{Molecular mass of NaBrO}_3}{5}$$

$$N_{\text{NaBrO}_3} = 5 M_{\text{NaBrO}_3}$$

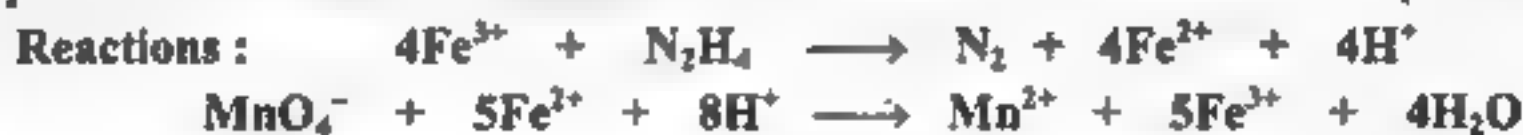
$$M_{\text{NaBrO}_3} = \frac{N_{\text{NaBrO}_3}}{5} = \frac{0.672}{5} = 0.1341 \text{ M.}$$

$$\text{Moles NaBrO}_3 \text{ in 85.5 mL of 0.1341 M solution} = 0.1341 \text{ M} \times (85.5/1000 \text{ litres})$$

$$\begin{aligned} \text{Weight of NaBrO}_3 \text{ required} &= 0.1341 \times (85.5/1000) \text{ mol} \times 151 \text{ g/mol} \\ &= 1.7313 \text{ g.} \end{aligned}$$

(b) A sample of hydrazine sulphate ($\text{N}_2\text{H}_4\text{SO}_4$) was dissolved in 100 mL of water. 10 mL of this solution was made to react with excess of ferric chloride solution and

warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 mL of M/50 potassium permanganate solution. Estimate the amount of hydrazine sulphate in one litre of the solution. (IIT/JEE 1988)



$$(b) \quad \text{Equivalent mass of KMnO}_4 = \frac{\text{Molecular mass of KMnO}_4}{5}$$

$$\begin{aligned}N_{\text{KMnO}_4} &= 5 M_{\text{KMnO}_4} \\ &= 5 \times \frac{M}{50} = 0.1 \text{ N}\end{aligned}$$

$$\text{Milli-equivalent in 20 mL of 0.1 N KMnO}_4 = 0.1 \text{ N} \times 20 \text{ mL} = 2 \text{ mequiv.}$$

∴ According to the law of equivalents :

$$\text{Milli-equivalents of Fe}^{2+} \text{ in 10 mL solution} = 2 \text{ mequiv} = 2 \times 10^{-3} \text{ equiv.}$$

$$\text{Equivalent mass of Fe}^{2+} = \frac{\text{Molecular mass of Fe}^{2+}}{1}$$

$$\text{Moles of Fe}^{2+} \text{ titrated} = 2 \times 10^{-3} \text{ mol}$$



$$\begin{aligned}\text{Molecular mass of N}_2\text{H}_6\text{SO}_4 &= 2 \times 14 + 6 \times 1 + 32 + 4 \times 16 \\ &= 130 \text{ g/mol.}\end{aligned}$$

4 mol Fe²⁺ is produced from 130 g N₂H₆SO₄.

Problem 31. An equal volume of a reducing agent is titrated separately with 1 M KMnO₄ in acid, neutral and alkaline media. The volumes of KMnO₄ required are 20 mL in acid, 33.4 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half reactions. Find out the volume of 1 M K₂Cr₂O₇ consumed, if the same volume of the reducing agent is titrated in an acid medium. (IIT/JEE 1989)

Solution. (a) For the titration of KMnO₄ against a reducing agent, one MnO₄⁻ accepts five electrons :



$$N_{\text{KMnO}_4} = n M_{\text{KMnO}_4}$$

$$N_{\text{KMnO}_4} = 5 M_{\text{KMnO}_4} = 5 \times 1 M_{\text{KMnO}_4} = 5\text{N.}$$

Let N₁, N₂ and N₃ be the normalities of the same KMnO₄ in acidic, neutral and alkaline medium. As equal volume of the reducing agent is titrated separately in all the cases, the same equivalent of KMnO₄ is used in each titration.

$$\text{Since } \quad \text{Milli-equivalent of KMnO}_4 = N_{\text{KMnO}_4} \times V \text{ in mL}$$

$$\therefore \quad (20 \text{ mL}) N_1 = (33.4 \text{ mL}) N_2 = (100 \text{ mL}) N_3 \quad \dots(i)$$

Solving eq. (i), we have

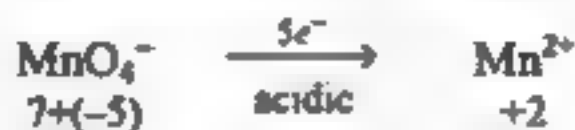
$$(20 \text{ mL}) N_1 = (33.4 \text{ mL}) N_2$$

$$\text{or} \quad N_2 = \frac{20 \text{ mL}}{33.4 \text{ mL}} \times N_1 = \frac{20}{33.4} \times 5\text{N} = 3\text{N}$$

$$(20 \text{ mL}) N_1 = (100 \text{ mL}) N_2$$

$$N_2 = \frac{20 \text{ mL}}{100 \text{ mL}} \times N_1 = \frac{20}{100} \times 5N = 1N.$$

In acid medium normality of KMnO_4 is 5N and 5 electrons are accepted by one MnO_4^- ion. In neutral medium, N_{KMnO_4} is 3N and therefore 3 electrons are accepted by 1 MnO_4^- . In alkaline medium, N_{KMnO_4} is 1N and therefore 1 electron is accepted by one MnO_4^- ion.



The oxidation state of manganese in the reduction product is +2 (acid medium), +4 (neutral medium) and +6 (alkaline medium).

The balanced chemical equations are :



For the reduction of potassium dichromate in the acid medium :



$$N_{\text{K}_2\text{Cr}_2\text{O}_7} = 6 M_{\text{K}_2\text{Cr}_2\text{O}_7}$$

$$N_{\text{K}_2\text{Cr}_2\text{O}_7} = 6 \times 1 M = 6 N$$

$$\text{Equivalent of reducing agent} = \text{Equiv. of } \text{K}_2\text{Cr}_2\text{O}_7 = \text{Equiv. of } \text{KMnO}_4$$

$$V \text{ mL} \times 6 N_{\text{K}_2\text{Cr}_2\text{O}_7} = 20 \text{ mL} \times 5 N_{\text{KMnO}_4}$$

$$V = \frac{20 \text{ mL} \times 5 N}{6 N} = 16.7 \text{ mL.}$$

Problem 32. A solution of 0.2 g of a compound containing Cu^{2+} and $\text{C}_2\text{O}_4^{2-}$ ions on titration with 0.02 M KMnO_4 in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralized with Na_2CO_3 , acidified with dil. acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 M $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete reduction. Find out the mole ratio of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ in the compound. Write down the balanced redox reactions involved in the above titrations.

(IIT/JEE 1991)



$$\text{Millimoles of } \text{KMnO}_4 \text{ used} = \text{Molarity} \times V \text{ in mL}$$

$$= 0.02 M \times 22.6 \text{ mL} = 0.452 \text{ mmol}$$



$$0.452 \text{ mmol } \text{KMnO}_4 = \frac{5}{2} \times 0.452 \text{ mmol } \text{C}_2\text{O}_4^{2-}$$

$$= 1.13 \text{ m mol } \text{C}_2\text{O}_4^{2-}$$



$$1 \text{ mol } \text{I}_2 = 2 \text{ mol } \text{Cu}^{2+} = 2 \text{ mol } \text{S}_2\text{O}_3^{2-}$$

$$1 \text{ mol } \text{Cu}^{2+} = 1 \text{ mol } \text{S}_2\text{O}_3^{2-}$$

$$\text{Milli-moles of } \text{Na}_2\text{S}_2\text{O}_3 \text{ used} = \text{Molarity} \times \text{Volume in mL}$$

$$= 0.05 \text{ M} \times 11.3 \text{ mL } \text{Cu}^{2+}$$

$$= 0.565 \text{ m mol } \text{Cu}^{2+}$$

$$\text{Cu}^{2+} : \text{C}_2\text{O}_4^{2-} = 0.565 \text{ m mol } \text{Cu}^{2+} : 1.13 \text{ m mol } \text{C}_2\text{O}_4^{2-}$$

$$= 1 \text{ Cu}^{2+} : 2 \text{ C}_2\text{O}_4^{2-}$$

Problem 33. A 1.0 g sample of Fe_2O_3 solid of 55.2 percent purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. (IIT/JEE 1991)

Solution. Amount of pure iron 1.0 g of Fe_2O_3

$$= \frac{\% \text{ Purity}}{100} \times \frac{\text{mass of } \text{Fe}_2\text{O}_3}{\text{molar mass of Fe}} \times \frac{2 \text{ molar mass of iron}}{\text{molar mass of } \text{Fe}_2\text{O}_3}$$

$$= \frac{55.2}{100} \times \frac{1.0 \text{ g}}{55.9} \times \frac{2 \times 55.9}{159.8} = 0.0069 \text{ mol} = 69 \text{ m mol}$$

$$\therefore \text{Moles of } \text{Fe}^{2+} \text{ in 100 mL solution} = 69 \text{ m mol}$$

$$\text{Moles of } \text{Fe}^{2+} \text{ in 25 mL solution} = 69 \text{ m mol} \times \frac{25 \text{ mL}}{100 \text{ mL}} = 17.25 \text{ m mol}$$

For the oxidation of Fe^{2+} to Fe^{3+} , 1 electron is lost



$$\text{Molecular mass of } \text{Fe}^{2+} = \text{Equivalent mass of } \text{Fe}^{2+}$$

$$17.25 \text{ m mol } \text{Fe}^{2+} = 17.25 \text{ milli-equivalent } \text{Fe}^{2+}$$

$$\text{Amount of oxidant used} = \text{molarity} \times \text{volume in mL}$$

$$= 0.0167 \text{ M} \times 17.0 = 0.2839 \text{ m mol}$$

$$\begin{aligned} \text{Number of electrons taken by the oxidant} &= \frac{\text{Molar mass}}{\text{Equivalent mass}} \\ &= \frac{\text{Number of equivalents}}{\text{Number of moles}} \\ &= \frac{17.25 \text{ milli-equivalent}}{0.2839 \text{ milli-mol}} = 6 \end{aligned}$$

Problem 34. A 0.56 gm sample of limestone is dissolved in acid and the calcium is precipitated as calcium oxalate. The precipitate is filtered, washed with water and dissolved in dilute sulphuric acid. This solution required 40 mL of 0.25 N KMnO_4 solution for titration. Calculate the percentage of CaO in this limestone sample.

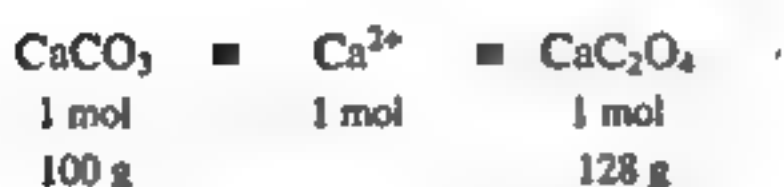
(At. wt. of $\text{Ca} = 40$) (Mol. wt. of $\text{KMnO}_4 = 158$)

(Roorkee 1992)



$$\begin{aligned}\text{Equivalent mass of calcium oxalate (CaC}_2\text{O}_4) &= \frac{\text{Molecular mass}}{2} \\ &= \frac{128}{2} = 64 \text{ g/equiv.}\end{aligned}$$

$$\begin{aligned}40 \text{ mL of } 0.25 \text{ N KMnO}_4 &= 40 \text{ mL of } 0.25 \text{ N CaC}_2\text{O}_4 \\ &= \frac{40 \text{ mL} \times 0.25 \text{ N}}{1000} \text{ equiv CaC}_2\text{O}_4 \\ &= \frac{40 \times 0.25}{1000} \times 64 = 0.64 \text{ g}\end{aligned}$$

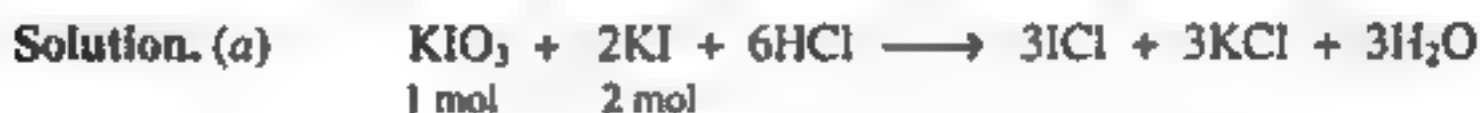


$$128 \text{ g CaC}_2\text{O}_4 = 100 \text{ g CaCO}_3$$

$$0.64 \text{ g CaC}_2\text{O}_4 = \frac{100 \text{ g}}{128 \text{ g}} \times 0.64 \text{ g} = 0.5 \text{ g CaCO}_3$$

$$\begin{aligned}\text{Percentage of CaCO}_3 &= \frac{\text{Amount of CaCO}_3}{\text{Mass of lime stone}} \times 100 \\ &= \frac{0.5 \text{ g}}{0.56 \text{ g}} \times 100 = 89.3\%.\end{aligned}$$

Problem 35. One gram of commercial AgNO_3 is dissolved in 50 mL of water. It is treated with 50 mL of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10) KIO_3 solution in presence of 6M HCl till all I^- ions are converted into ICl . It requires 50 mL of (M/10) KIO_3 solution. Twenty millilitres of the same stock solution of KI requires 30 mL of (M/10) KIO_3 under similar conditions. Calculate the percentage of AgNO_3 in the sample.



$$2 \text{ mol KI} = 1 \text{ mol KIO}_3$$

$$\text{Moles of KIO}_3 = \text{Volume in litres} \times \text{Molarity}$$

$$= \frac{30}{1000} \text{ L} \times \frac{\text{M}}{10}$$

$$\text{Moles of KI} = \frac{30}{1000} \times \frac{\text{M}}{10} \times 2$$

$$20 \text{ mL of stock KI solution} = 30 \text{ mL of } \frac{\text{M}}{10} \text{ KIO}_3$$

$$\text{Molarity of KI solution} = \frac{30}{1000} \times \frac{\text{M}}{10} \times 2 \times \frac{1000}{20} = \frac{3}{10} \text{ M}$$

$$\text{Millimoles of KI in 50 mL of KI solution} = \text{Volume in mL} \times \text{Molarity}$$

$$= 50 \text{ mL} \times \frac{3}{10} \text{ M} = 15 \text{ mmol}$$

$$50 \text{ mL of } \frac{\text{M}}{10} \text{ KIO}_3 \text{ solution} = 50 \text{ mL} \frac{\text{M}}{10} \times 2\text{KI} = 10 \text{ mmol}$$

$$\therefore \text{ Millimoles of KI that react with AgNO}_3 = 15 - 10 = 5 \text{ mmol} = \frac{5}{1000} \text{ mol}$$

$$\text{Molecular mass of AgNO}_3 = 108 + 14 + 3 \times 16 = 170 \text{ g/mol}$$

$$\text{Mass of AgNO}_3 \text{ in solution} = \text{Moles of AgNO}_3 \times \text{Molar mass}$$

$$= \frac{5}{1000} \text{ mol} \times 170 \text{ g/mol} = 0.85 \text{ g}$$

$$\% \text{ AgNO}_3 \text{ in the sample} = \frac{0.85}{1 \text{ g}} \times 100 = 85\%.$$

Problem 36. In an ore the only oxidizable material is Sn^{2+} . This ore is titrated with a dichromate solution containing 2.5 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.50 litre. A 0.40 g sample of the ore required 10.0 cm^3 of titrant to reach equivalence point. Calculate the percentage of tin in ore. (K = 39.1, Cr = 52, Sn = 118.7) (Roorkee 1993)

Solution.



$$\text{Molecular mass of } \text{K}_2\text{Cr}_2\text{O}_7 = 2 \times 39.1 + 2 \times 52 + 7 \times 16 = 294.2 \text{ g/mol}^{-1}$$

Molarity of $\text{K}_2\text{Cr}_2\text{O}_7$ solution

$$= \frac{\text{Mass of } \text{K}_2\text{Cr}_2\text{O}_7}{\text{Molecular mass of } \text{K}_2\text{Cr}_2\text{O}_7 \times \text{litres of solution}}$$

$$= \frac{2.5 \text{ g}}{294.2 \text{ g mol}^{-1}} \times \frac{1}{0.5 \text{ L}} = 0.017 \text{ M}$$

$$\begin{aligned} \text{Moles of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ used at the equivalence point} &= \text{Molarity} \times \text{Volume used in litres} \\ &= 0.017 \text{ M} \times (10.0/1000) \text{ L} \\ &= 0.00017 \text{ moles } \text{K}_2\text{Cr}_2\text{O}_7 \end{aligned}$$

From the balanced chemical equation :



$$\begin{aligned} 0.00017 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 &= \frac{3 \text{ mol } \text{Sn}^{2+} \times 0.00017 \text{ mol}}{1 \text{ mol}} \\ &= 0.00051 \text{ mol } \text{Sn}^{2+} \end{aligned}$$

$$\begin{aligned} \text{Mass of tin in the ore} &= \text{moles of tin} \times \text{atomic mass of tin} \\ &= 0.00051 \text{ mol} \times 118.7 \text{ g mol}^{-1} = 0.0605 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Percentage of tin in the ore} &= \frac{\text{Mass of tin}}{\text{Mass of ore}} \times 100 \\ &= \frac{0.0605 \text{ g}}{0.40 \text{ g}} \times 100 = 15.1\%. \end{aligned}$$

Problem 37. A 0.5 g sample containing MnO_2 is treated with HCl , liberating Cl_2 . The Cl_2 passed into a solution of KI and 30.0 cm^3 of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ are required to titrate

the liberated iodine. Calculate the percentage of MnO_2 in the sample.

(At. wt. of Mn = 55).

(Roorkee 1994)

Solution.



Millimoles of $\text{Na}_2\text{S}_2\text{O}_3$ in 30 cm^3 of $0.1 \text{ M } \text{Na}_2\text{S}_2\text{O}_3 = 0.1 \text{ M} \times 30 \text{ cm}^3 = 3 \text{ millimoles}$

$$3 \text{ millimoles of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{1 \text{ mol } \text{MnO}_2}{2 \text{ mol } \text{Na}_2\text{S}_2\text{O}_3} \times 3 \text{ millimoles } \text{Na}_2\text{S}_2\text{O}_3$$

$$= 1.5 \text{ millimoles } \text{MnO}_2$$

$$= \frac{1.5}{1000} \text{ mol} \times \text{Mol. mass of } \text{MnO}_2$$

$$= \frac{1.5}{1000} \text{ mol} \times 87 \text{ g/mol} = 0.1305 \text{ g}$$

$$\% \text{MnO}_2 = \frac{\text{Mass of } \text{MnO}_2 \times 100}{\text{Mass of sample}}$$

$$= \frac{0.1305 \text{ g}}{0.5 \text{ g}} \times 100 = 26.1\%$$

Problem 38. 0.5 g mixture of $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 was treated with excess of KI in acidic medium. Iodine liberated required 100 cm^3 of 0.15 N sodium thiosulphate solution for titration. Find the percent amount of each in the mixture.

(At. wt. K = 39, Cr = 52, Mn = 55, Na = 23, S = 32)

(Roorkee 1995)

Solution.



$$\begin{aligned} \text{Molecular mass of } \text{K}_2\text{Cr}_2\text{O}_7 &= 2 \times 39 + 2 \times 52 + 7 \times 16 \\ &= 284 \text{ g/mol} \end{aligned}$$

$$\text{Molecular mass of } \text{KMnO}_4 = 39 + 55 + 4 \times 16 = 158 \text{ g/mol}$$

$$\begin{aligned} \text{Equivalent mass of } \text{K}_2\text{Cr}_2\text{O}_7 &= \frac{\text{Molecular Mass of } \text{K}_2\text{Cr}_2\text{O}_7}{\text{Number of electrons gained}} \\ &= \frac{284}{6} = 47.3 \text{ g/equiv.} \end{aligned}$$

$$\begin{aligned} \text{Equivalent mass of } \text{KMnO}_4 &= \frac{\text{Molecular mass of } \text{KMnO}_4}{\text{Number of electrons gained}} \\ &= \frac{158}{5} = 31.6 \text{ g/equiv.} \end{aligned}$$

Let the mass of $\text{K}_2\text{Cr}_2\text{O}_7$ in the mixture = $x \text{ g}$

\therefore Mass of KMnO_4 in the mixture = $(0.5 - x) \text{ g}$

$$\text{Gram-equivalent of } K_2Cr_2O_7 = \frac{x}{47.3} \text{ equiv.}$$

$$\text{Gram-equivalent of } KMnO_4 = \frac{0.5 - x}{31.6} \text{ equiv.}$$

$$\text{Total gram-equivalents} = \frac{x}{47.3} + \frac{(0.5 - x)}{31.6}$$

Gram-equivalent of $Na_2S_2O_3$ in 100 cm^3 of $0.15 \text{ N } Na_2S_2O_3$

$$= 0.15 \text{ N} \times \left(\frac{100}{1000} \right) \text{ L} = 0.015 \text{ equiv.}$$

According to the law of normalities,

$$\frac{x}{47.3} + \frac{0.5 - x}{31.6} = 0.015$$

$$x = 0.078 \text{ g}$$

$$\% \text{ amount } K_2Cr_2O_7 = \frac{0.078 \text{ g}}{0.5 \text{ g}} \times 100\% = 15.6\%$$

$$\% \text{ amount of } KMnO_4 = 100\% - 15.6 = 84.4\%$$

Problem 39. 1.6 g of pyrolusite ore was treated with 50 cm^3 of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 cm^3 in a flask. 25 cm^3 of this solution when titrated with $0.1 \text{ N } KMnO_4$ required 32 cm^3 of the solution. Find out the percentage of pure MnO_2 in the sample and also the percentage of available oxygen. (Atomic weight of $Mn = 54.9$) (Roorkee 1996)

Solution. Milli-equiv. of oxalic acid = $50 \text{ cm}^3 \times 1.0 \text{ N} = 50 \text{ m eq.}$

$$N_1 V_1 = N_2 V_2$$

$$N_1 = \frac{N_2 V_2}{V_1} = \frac{32 \text{ cm}^3 \times 0.1 \text{ N}}{25 \text{ cm}^3}$$

$$\begin{aligned} \text{Milli-equiv. of oxalic acid left in } 25 \text{ cm}^3 &= \frac{32 \text{ cm}^3 \times 0.1 \text{ N}}{25 \text{ cm}^3} \times 25 \text{ cm}^3 \\ &= 3.2 \text{ m eq.} \end{aligned}$$

$$\text{Milli-equiv. of oxalic acid left in } 250 \text{ cm}^3 = \frac{3.2 \text{ m eq.} \times 250 \text{ cm}^3}{25 \text{ cm}^3} = 32 \text{ m eq.}$$

$$\begin{aligned} \text{Milli-equiv. of } MnO_2 &= \text{Milli-equiv. of oxalic acid added} - \\ &\quad \text{Milli-equiv. of oxalic acid left} \\ &= 50 \text{ m eq} - 32 \text{ m eq} = 18 \text{ m eq} \end{aligned}$$



$$18 \text{ m equiv.} = \frac{18}{2} \text{ m eq.} = 9 \text{ m mol} = 9 \times 10^{-3} \text{ mol}$$

$$\text{Molecular mass of } MnO_2 = 54.9 + 32 = 86.9 \text{ g/mol}$$

$$\begin{aligned} \text{Mass of } MnO_2 &= \text{Number of moles} \times \text{Molecular mass} \\ &= 9 \times 10^{-3} \text{ mol} \times 86.9 \text{ g/mol} = 0.7821 \text{ g} \end{aligned}$$

$$\begin{aligned}\% \text{ of MnO}_2 &= \frac{\text{Mass of MnO}_2}{\text{Mass of the ore}} \times 100 \\ &= \frac{0.7821 \text{ g}}{1.6 \text{ g}} \times 100 = 48.88 \%\end{aligned}$$

$$\begin{array}{rcl}\text{MnO}_2 & = & 2\text{O} \\ 86.9 \text{ g} & & 32 \text{ g}\end{array}$$

$$\text{Mass of available O}_2 = 9 \times 10^{-3} \times 32 \text{ g} = 0.288 \text{ g}$$

$$\% \text{ of available O}_2 = \frac{0.288 \text{ g}}{1.6 \text{ g}} \times 100 = 18\%$$

Problem 40. A 3.00 g sample containing Fe_3O_4 , Fe_2O_3 and an inert impure substance is treated with excess of KI solution in presence of dilute H_2SO_4 . The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution requires 11.0 mL of 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$ solution to reduce the iodine present. A 50 mL of the diluted solution, after complete extraction of the iodine requires 12.80 mL of 0.25 M KMnO_4 solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+} . Calculate the percentage of Fe_2O_3 and Fe_3O_4 in the original sample. (IIT/JEE 1996)

Solution. I^- reduces Fe^{3+} to Fe^{2+}



$$\begin{aligned}\text{(i)} \quad \text{Molecular mass of Na}_2\text{S}_2\text{O}_3 &= \text{Equivalent mass of Na}_2\text{S}_2\text{O}_3 \\ 0.5 \text{ M Na}_2\text{S}_2\text{O}_3 &= 0.5 \text{ N Na}_2\text{S}_2\text{O}_3\end{aligned}$$

$$\text{Milli-equivalents in 11.0 mL of 0.5 N Na}_2\text{S}_2\text{O}_3 = 11 \times 0.5 = 5.5 \text{ m equiv.}$$

$$\begin{aligned}\text{Milli-equivalents of Na}_2\text{S}_2\text{O}_3 &= \text{Milli-equivalents of I}^- \\ &= \text{Milli-equivalents of Fe}^{3+} \text{ in 100 mL solution} \\ &= 5.5 \times \frac{100 \text{ mL}}{20 \text{ mL}} = 27.5 \text{ m eq. Fe}^{3+} \\ &= 27.5 \text{ m eq.}\end{aligned}$$



$$\text{Equivalent mass of KMnO}_4 = \frac{\text{Molecular mass of KMnO}_4}{5}$$

$$0.25 \text{ M KMnO}_4 = 5 \times 0.250 = 1.25 \text{ N KMnO}_4$$

$$\begin{aligned}\text{Milli-equivalent in 12.80 mL of 1.25 N KMnO}_4 \\ &= 12.80 \times 1.25 = 16.0 \text{ m equiv.}\end{aligned}$$

$$\begin{aligned}\text{Milli equivalent of KMnO}_4 &= \text{Milli-equiv of Fe}^{2+} \text{ in 100 mL solution} \\ &= 16.0 \times \frac{100}{50} = 32 \text{ m eq.} = 32 \text{ m mol}\end{aligned}$$

Fe_3O_4 is a mixture of FeO and Fe_2O_3 in the ratio (1:2)

$$\text{Moles of Fe}_2\text{O}_3 = \frac{27.5}{2} = 13.75 \text{ m mol}$$

$$\text{Moles of FeO in Fe}_3\text{O}_4 = 32 - 27.5 = 4.5 \text{ m mol}$$

$$\begin{aligned}\text{Mass of Fe}_3\text{O}_4 &= \frac{4.5}{1000} \text{ m mol} \times \text{mol. mass of Fe}_3\text{O}_4 \\ &= \frac{4.5}{100} \text{ mol} \times 232 = 1.044 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Millimoles of Fe}_2\text{O}_3 \text{ existing separately} &= 13.75 \text{ m mol} - 4.5 \text{ m mol} \\ &= 9.25 \text{ m mol}\end{aligned}$$

$$\text{Mass of Fe}_2\text{O}_3 = \frac{9.25 \text{ m mol}}{1000} \times \text{Mol mass of Fe}_2\text{O}_3$$

$$\text{Mass of Fe}_2\text{O}_3 = \frac{9.25}{1000} \times 160 = 1.48 \text{ g}$$

$$\% \text{ Fe}_3\text{O}_4 = \frac{\text{Mass of Fe}_3\text{O}_4}{\text{Mass of Mixture}} \times 100$$

$$= \frac{1.044 \text{ g}}{3 \text{ g}} \times 100 = 34.8\%$$

$$\% \text{ Fe}_2\text{O}_3 = \frac{\text{Mass of Fe}_2\text{O}_3 \times 100}{\text{Mass of Mixture}}$$

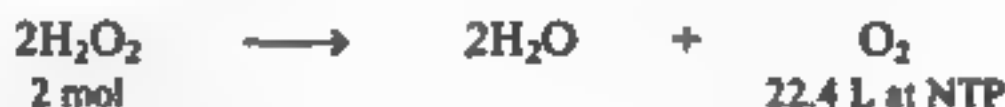
$$= \frac{1.48 \text{ g}}{3 \text{ g}} \times 100 = 49.33\%.$$

Problem 41. To a 25 mL H_2O_2 solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H_2O_2 solution. (IIT/JEE 1997)

$$\text{Solution.} \quad \frac{20}{1000} \text{ L} \times 0.3 \text{ N} = 6 \times 10^{-3} \text{ equiv Na}_2\text{S}_2\text{O}_3 = 6 \times 10^{-3} \text{ equiv.}$$

$$\text{H}_2\text{O}_2 = 6/2 \times 10^{-3} \text{ mol H}_2\text{O}_2$$

$$\text{Moles of H}_2\text{O}_2 \text{ in 1 cm}^3 \text{ solution} = \frac{6}{2} \times \frac{10^{-3}}{25} = \frac{3}{25} \times 10^{-3} \text{ mol}$$



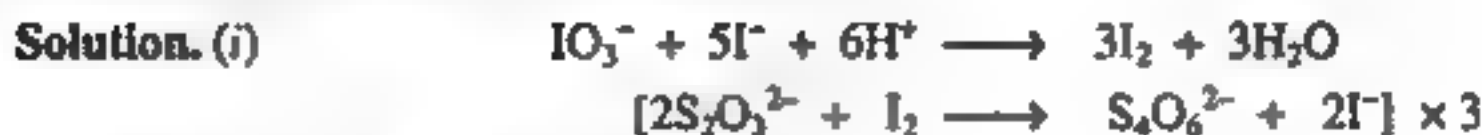
2 mol H_2O_2 produces 22400 mL at NTP

$$\frac{3}{25} \times 10^{-3} \text{ mol produces} = \frac{22400}{2} \times \frac{3 \times 10^{-3}}{25} = 1.344 \text{ mL}$$

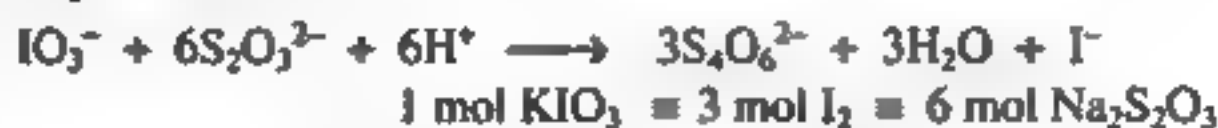
\therefore Volume strength of H_2O_2 solution is 1.344 V.

Problem 42. An aqueous solution containing 0.10 kg KIO_3 (formula wt. = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

(IIT/JEE 1998)



From the above equations :

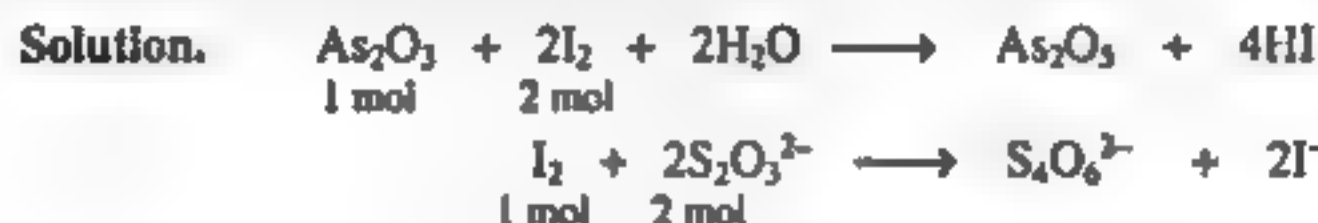


$$\frac{0.10 \text{ g}}{214.0 \text{ g/mol}} \text{ KIO}_3 \equiv \frac{6 \times 0.10}{214} \text{ mol Na}_2\text{S}_2\text{O}_3$$

$$45 \text{ mL solution contains } \frac{6 \times 0.10}{214} \text{ mol Na}_2\text{S}_2\text{O}_3$$

$$1000 \text{ mL solution contains } \frac{6 \times 0.10}{214} \times \frac{1000}{45} = 0.0623 \text{ M Na}_2\text{S}_2\text{O}_3$$

Problem 43. 12 g of an impure sample of arsenious oxide was dissolved in water containing 7.5 g of sodium bicarbonate and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidised by 22.4 mL of a solution of iodine. 25 mL of this iodine solution reacted with same volume of a solution containing 24.8 g of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in one litre. Calculate the percentage of arsenious oxide in the sample. (Atomic mass of As = 75). (IIT/JEE 1999)



$$\text{Molarity of Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O solution} = \frac{\text{Mass of Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O per litre}}{\text{Molecular mass}}$$

$$= \frac{24.8 \text{ g}}{248 \text{ g}} = 0.1 \text{ M}$$

$$\text{Millimoles of I}_2 \text{ in 25 mL} = \frac{1}{2} \times \text{millimoles of Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$$

$$= \frac{1}{2} \times 25 \text{ mL} \times 0.1 \text{ M} = 1.25 \text{ m mol}$$

$$\text{Millimoles of I}_2 \text{ in 22.4 mL} = \frac{1.25}{25} \times 22.4$$

$$= \frac{1}{2} \times \frac{1.25}{25} \times 22.4 \text{ m mol As}_2\text{O}_3$$

$$\text{Millimoles of As}_2\text{O}_3 \text{ in 250 mL} = \frac{1}{2} \times \frac{1.25}{25} \times 22.4 \times \frac{250}{25}$$

$$= 5.6 \text{ m mol} = 5.6 \times 10^{-3} \text{ mol}$$

$$= 5.6 \times 10^{-3} \text{ m mol} \times 198 \text{ g/mol}$$

$$(\because \text{molecular mass of As}_2\text{O}_3 = 198)$$

$$= 1.1088 \text{ g}$$

$$\% \text{ of As}_2\text{O}_3 \text{ in the sample} = \frac{\text{Mass of As}_2\text{O}_3}{\text{Mass of impure As}_2\text{O}_3} \times 100$$

$$= \frac{1.1088 \text{ g}}{12 \text{ g}} \times 100 = 9.24\%$$



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16. How many equivalents are present in 20 g Pb_3O_4 in the solution.



$$[\text{Hint : Equivalent mass} = \frac{\text{Molecular mass}}{2}]$$

$$\text{Change in oxidation number} = 8 - 6 = 2$$

17. 25 millilitres of a 0.001 N KMnO_4 containing sulphuric acid at 40°C required 20 mL of a nitrite solution for the end-point.



- (a) What is the normality of NO_2^- ?
 (b) What is the strength of NO_2^- in grams per litre ?
 18. A solution containing x grams of H_2O_2 requires for titration 14.05 mL of 0.003 M KMnO_4 solution.



- (a) What is the value of x ?
 (b) What is the mass of O_2 evolved during titration ?
 (c) How many millilitres of dry oxygen are measured under standard conditions ?
 19. 0.4 g sample of steel containing manganese as an impurity is analysed by sodium bismuthate method. The sample is dissolved in nitric acid and the resulting solution treated with excess sodium bismuthate to form permanganic acid. The sodium bismuthate was filtered and added to 40 mL of 0.025 N Mohr's salt solution to reduce permanganate to manganous salt. The resulting solution when titrated against 0.015 N KMnO_4 required 40 mL solution. Calculate the percentage of manganese in the steel sample.



20. 0.2 g sample of magnetite containing 20% Fe_2O_3 is fused with Na_2O_2 and the material leached with H_2O and acidified. The solution is then treated with amalgamated zinc to obtain all iron as ferrous. This solution required 10 mL of a KMnO_4 solution for titration. What is the molarity of KMnO_4 solution ?
 21. 0.1 g of an iron oxide was fused with KHSO_4 and then dissolved in an acid. The iron was then reduced to ferrous in solution. This solution required 12.96 mL of 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$ for complete oxidation. What is the formula of the oxide : FeO , Fe_2O_3 or Fe_3O_4 ?
 22. What is the iron value of 0.025 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution in acid medium ?
 23. Calculate the volume of $\text{K}_2\text{Cr}_2\text{O}_7$ solution (25.0 g/litre) required to completely oxidize 3.402 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in acid solution ?
 24. 0.1 g sample of chromite was brought into solution by fusion with excess of sodium peroxide.



The melt was dissolved in water and the impurities filtered off. This solution was acidified with dilute HCl and 1.2 g of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ added. The excess of ferrous salt required 12 mL of 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$ for titration. What is the percentage of chromium in the sample ?

25. 1 mL of a blood sample was diluted with water and calcium precipitated as calcium oxalate. The precipitate was filtered and then dissolved in H_2SO_4 . The solution required 1 mL of 0.005 N KMnO_4 for titration to the end-point. What is the concentration of Ca^{2+} in milligrams per millilitre of blood. ($\text{Ca} = 40$ amu)
26. 0.367 g of a mixture containing sodium oxalate and potassium oxalate requires 125 mL of 0.04 N KMnO_4 for titration to the end-point. What is the percentage of sodium oxalate in the mixture?
27. 3.92 g $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ were dissolved in enough water containing H_2SO_4 and the solution made up to 100 mL. 10 millilitre of this solution required 0.03326 g of 95% pure KMnO_4 crystals. Calculate the value of x .
28. How many grams of iodine (I_2) are required to react completely with 18.5 millilitre of 0.01 N $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution?
29. An excess of KI is added to a solution of potassium dichromate and the liberated iodine is titrated with 36.0 millilitres of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ using starch as the indicator. How many grams of $\text{K}_2\text{Cr}_2\text{O}_7$ were present in the dichromate solution?



30. 3.0 g of a steel were subjected to chemical treatment to convert sulphur into H_2S gas which when titrated required 1.20 mL of 0.04 N iodine solution. What is the percentage of sulphur in the steel?
31. 48.0 mL of a $\text{Na}_2\text{S}_2\text{O}_3$ solution is required to titrate the iodine liberated from excess KI by 0.3287 g of KIO_3 . What is the normality of sodium thiosulphate solution?
32. 0.32 g sample of impure KI was dissolved in 1.1 millimole of K_2CrO_4 and 25 ml of 5 N H_2SO_4 .

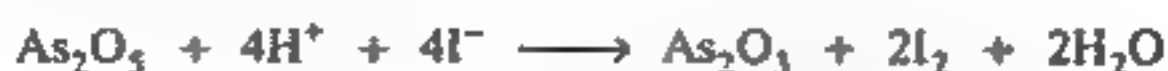


Iodine formed was expelled by boiling and the solution containing excess chromate was cooled, treated with excess KI and I_2 liberated when titrated required 14.0 mL of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. Calculate the percentage purity of the original KI sample.

33. A sample of pyrolusite weighing 0.8156 g was boiled with an excess of conc. HCl and the evolved Cl_2 passed into a solution of KI. The liberated I_2 required 1.86 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 50 mL of 0.15 N $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution. What is the percentage of pure MnO_2 in the sample?



34. 0.3521 g of a sample containing a mixture of KMnO_4 and K_2CrO_4 was treated with excess KI in acid solution and the I_2 liberated required 12.5 millilitres of 0.64 N $\text{Na}_2\text{S}_2\text{O}_3$ solution. What are the percentages of Mn and Cr in the mixture?
35. A mixture of As_2O_3 and As_2O_5 requires 20.10 mL of 0.05 N I_2 for titration. The resulting solution is then acidified and excess KI was added. The liberated I_2 required 1.1113 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ for complete reaction. What is the sum of the masses of As_2O_3 and As_2O_5 ?





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(b) For the reaction between BaCl_2 and Na_2SO_4 ,



the actual reaction is in between Ba^{2+} and SO_4^{2-} ions.



$$\therefore \text{Equivalent mass of } \text{BaCl}_2 = \frac{\text{Molecular mass of } \text{BaCl}_2}{\text{Charge on } \text{Ba}^{2+}}$$

$$= \frac{\text{Molecular mass of } \text{BaCl}_2}{2}$$

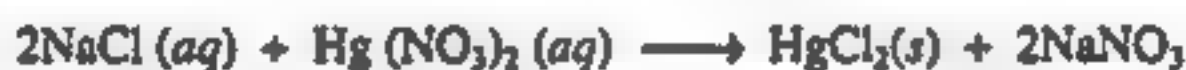
$$N_{\text{BaCl}_2} = 2M_{\text{BaCl}_2}$$

$$\text{Equivalent mass of } \text{Na}_2\text{SO}_4 = \frac{\text{Molecular mass of } \text{Na}_2\text{SO}_4}{\text{Charge on } \text{SO}_4^{2-}}$$

$$= \frac{\text{Molecular mass of } \text{Na}_2\text{SO}_4}{2}$$

$$N_{\text{Na}_2\text{SO}_4} = 2M_{\text{Na}_2\text{SO}_4}$$

(c) For the reaction between sodium chloride and mercuric nitrate acidified with nitric acid,



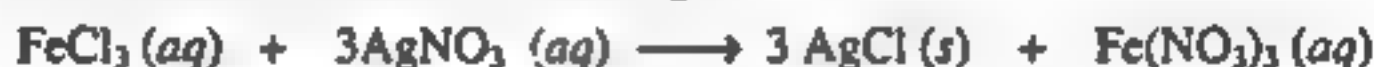
$$\text{Equivalent mass of } \text{Hg} (\text{NO}_3)_2 = \frac{\text{Molecular mass of } \text{Hg} (\text{NO}_3)_2}{2}$$

$$N_{\text{Hg} (\text{NO}_3)_2} = 2M_{\text{Hg} (\text{NO}_3)_2}$$

$$\text{Equivalent mass of } \text{NaCl} = \frac{\text{Molecular mass of } \text{NaCl}}{1}$$

$$N_{\text{NaCl}} = M_{\text{NaCl}}$$

(d) For the reaction between FeCl_3 and AgNO_3 ,



$$\text{Equivalent mass of } \text{FeCl}_3 = \frac{\text{Molecular mass of } \text{FeCl}_3}{3}$$

$$N_{\text{FeCl}_3} = 3M_{\text{FeCl}_3}$$

✓ SOLVED PROBLEMS

Problem 1. A piece of aluminium weighing 2.7 g is heated with 75.0 mL of sulphuric acid (sp. gr. 1.18 containing 24.7% H_2SO_4 by weight). After the metal is carefully dissolved, the solution is diluted to 400 mL. Calculate the molarity of the free H_2SO_4 in the resulting solution.

Solution. Mass of 75.0 mL of H_2SO_4 solution = $75 \times 1.18 = 88.5$ g

$$\text{Mass of } \text{H}_2\text{SO}_4 \text{ in this solution (24.7\%)} = \frac{24.7}{100} \times 88.5 = 21.85 \text{ g}$$



$$\text{Mass of H}_2\text{SO}_4 \text{ that reacts with 2.7 g Al} = \frac{294 \text{ g}}{54 \text{ g}} \times 2.7 \text{ g} = 14.7 \text{ g}$$

$$\text{Mass of unreacted H}_2\text{SO}_4 = 21.85 \text{ g} - 14.7 \text{ g} = 7.15 \text{ g}$$

$$\text{Strength of the diluted solution} = 7.15 \times \frac{1000}{400} = 17.875 \text{ g/litre}$$

$$\begin{aligned} \text{Molarity of H}_2\text{SO}_4 \text{ solution} &= \frac{\text{Mass H}_2\text{SO}_4/\text{Litre}}{\text{Molecular mass of H}_2\text{SO}_4} \\ &= \frac{17.875 \text{ g/Litre}}{98 \text{ g/mol}} = 0.182 \text{ M H}_2\text{SO}_4 \end{aligned}$$

Problem 2. A sample of magnesium metal containing some magnesium oxide as impurity was dissolved in 125 mL of 0.1 N H_2SO_4 . The volume of hydrogen evolved at 27.3°C and 1 atm was 120.1 mL. The resulting solution was found to be 0.02 N with respect to sulphuric acid. Calculate (i) the mass of sample dissolved and (ii) the percentage weight of magnesium in the sample. Neglect any change in the volume of the solution. ($\text{Mg} = 12.3 \text{ amu}$) (IIT/JEE 1977)

Solution. Mg reacts with H_2SO_4 to evolve H_2 gas whereas MgO dissolves in acid to form water.



$$\begin{aligned} \text{Equivalent mass of Mg} &= \frac{\text{Atomic mass of Mg}}{2} \\ &= \frac{24.3}{2} = 12.15 \text{ g/equiv.} \end{aligned}$$

$$\text{Molecular mass of MgO} = 24.3 + 16 = 40.3 \text{ amu}$$

$$\text{Volume of H}_2 \text{ at STP} = 120.1 \times \frac{273}{300.3} = 109.1 \text{ mL}$$

$$\text{Mass of H}_2 = \frac{2 \times 109.1}{22400} \text{ g H}_2$$

2 g H_2 is evolved from 24.3 g Mg

$$\frac{2 \times 109.1}{22400} \text{ g H}_2 \text{ is evolved from } \frac{2 \times 109.1}{22400} \times \frac{24.3}{2} = 0.1184 \text{ Mg}$$

$$\text{Equivalents of Mg} = \frac{0.1184}{12.15} = 0.00975$$

$$\begin{aligned} \text{Milli-equivalents H}_2\text{SO}_4 \text{ in 125 ml of 0.1 N H}_2\text{SO}_4 &= 0.1 \text{ N} \times 125 \text{ mL} = 12.5 \end{aligned}$$

$$\text{Milli-equivalents H}_2\text{SO}_4 \text{ left after the reaction} = 0.02 \text{ N} \times 125 \text{ mL} = 2.5$$

$$\begin{aligned} \text{Milli-equivalents H}_2\text{SO}_4 \text{ that reacted with (Mg + MgO)} &= 12.5 - 2.5 = 10 \\ &= 10 \end{aligned}$$

$$10 \text{ Milli-equivalents} = 10 \times 10^{-3} = 0.01 \text{ equivalents}$$

$$\therefore \text{Equivalents of MgO} = \text{Equivalents of H}_2\text{SO}_4 - \text{Equivalents of Mg} \\ = 0.01 - 0.00975 = 0.00025$$

$$\text{Mass of MgO} = \text{Equivalents} \times \text{Equivalent mass} \\ = 0.00025 \times \frac{40.3}{2} = 0.005 \text{ g}$$

$$\text{Mass of the sample} = \text{Mass Mg} + \text{Mass MgO} \\ = 0.1184 + 0.005 = 0.1234 \text{ g}$$

$$\text{Percent by weight, Mg} = \frac{0.1184 \text{ g}}{0.1234 \text{ g}} \times 100 = 95.95\% \text{ Mg.}$$

Problem 3. A polyvalent metal weighing 0.100 g and having atomic weight 51.0 reacted with dil H_2SO_4 to give 43.9 ml of hydrogen at STP. This solution containing the metal in the lower oxidation state was found to require 58.8 mL of 0.1 N permanganate for complete oxidation. What are the valencies of the metal? (IIT/JEE 1977)

Solution. 43.9 mL H_2 at STP \equiv 0.100 g metal

$$11200 \text{ mL H}_2 \text{ (1 gram-equivalent)} \equiv \frac{0.100 \text{ g}}{43.9 \text{ mL}} \times 11200 \text{ mL} = 25.5 \text{ g}$$

Valency of the metal in the lower oxidation state

$$= \frac{\text{Atomic mass}}{\text{Equivalent mass}} = \frac{51.0}{25.5} = 2$$

58.8 mL of 0.1 N $\text{KMnO}_4 \equiv$ gram-equivalents of M^{2+}

$$= 0.1 \text{ N} \times \left(\frac{58.8}{1000} \right) \text{ litre} \\ = 0.00588 \text{ equivalents M}^{2+}$$

$$\frac{0.100 \text{ g M}^{2+}}{\text{Equivalent mass of M}^{2+}} = 0.00588 \text{ equiv.}$$

$$\text{Equivalent mass of M}^{2+} = \frac{0.100 \text{ g}}{0.00588 \text{ equiv.}} = 17.0 \text{ g/equiv.}$$



$$\text{Equivalent mass} = \frac{\text{Atomic mass of M}^{2+}}{n}$$

$$n = \frac{51}{17} = 3$$

\therefore The valency of the metal in the higher oxidation state $= n + 2 = 3 + 2 = 5$

Problem 4. (a) A zinc rod weighing 25 g was kept in 100 mL of 1 M CuSO_4 solution. After a certain time the molarity of Cu^{2+} in the solution was 0.8. What was the molarity of the sulphate (SO_4^{2-})? What was the weight of zinc rod after cleaning?

(b) If the above experiment is done with copper rod of weight 25 g and 50 mL of 2 M ZnSO_4 solution, what would be the molarity of Zn^{2+} at the end of the same interval? ($\text{Zn} = 65.4$; $\text{Cu} = 63.5$) (IIT/JEE 1976)

Solution. (a) Zinc is more reactive than copper,





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Solution. (a)

Moles = Molarity \times Volume in litres

$$\text{Moles of BaCl}_2 = 0.3 \text{ M} \times \frac{55}{1000} \text{ litre} = 0.0165 \text{ mol}$$

(b)

1 mole $\text{BaCl}_2 = 2$ moles Cl^-

$$0.0165 \text{ moles BaCl}_2 = 2 \times 0.0165 \text{ mol} = 0.033 \text{ mol Cl}^-$$

Problem 7. How many grams of AgNO_3 should be dissolved to make 350 mL of 0.15 M AgNO_3 solution ? $\text{Ag} = 108$ amu.

Solution. Molecular mass of $\text{AgNO}_3 = 108 + 14 + 3 \times 16 = 170$ amu

$$\text{Moles of AgNO}_3 \text{ required} = 0.15 \text{ M} \times \frac{350}{1000} \text{ litre}$$

$$\text{Mass of AgNO}_3 \text{ required} = 0.15 \times \frac{350}{1000} \times 170 = 8.925 \text{ g AgNO}_3$$

$$\text{or} \quad 0.15 = \frac{W_R}{170} \times \frac{1000}{350} \quad \text{or} \quad W_R = \frac{0.15 \times 170 \times 350}{1000} = 8.925 \text{ g}$$

Problem 8. 25 mL of a BaCl_2 solution required 35 mL of 0.1 N AgNO_3 for titration using potassium chromate as the indicator to the faint reddish brown end-point. (a) What is the normality of the BaCl_2 solution. (b) What is its concentration in grams per litre ? ($\text{Ba} = 137.3$ amu)

Solution. (a) $N_{\text{BaCl}_2} \times V_{\text{BaCl}_2} = N_{\text{AgNO}_3} \times V_{\text{AgNO}_3}$

$$N_{\text{BaCl}_2} = 0.1 \text{ N} \times \frac{35 \text{ mL}}{25 \text{ mL}} = 0.14 \text{ N}$$

(b)



$$\text{Equivalent mass of BaCl}_2 = \frac{\text{Molecular mass of BaCl}_2}{2} = \frac{137.3}{2} \text{ g/equiv.}$$

$$\text{Concentration of BaCl}_2 = \frac{0.14 \times 137.3}{2} = 9.611 \text{ g/litre BaCl}_2.$$

Problem 9. How many mL of 0.15 M CaCl_2 are needed to completely react with 25 mL of 0.1 M AgNO_3 solution to precipitate AgCl ? What species are present in the final solution and what are their concentrations ?

Solution.

Millimoles of AgNO_3 in 25 mL of 0.1 M $\text{AgNO}_3 = 0.1 \text{ M} \times 25 \text{ mL}$

$$= 2.5 \text{ millimoles Ag}^+$$



$$1 \text{ mole Ag}^+ = 1 \text{ mole Cl}^-$$

$$0.15 \text{ M CaCl}_2 = 2 \times 0.15 \text{ M Cl}^- = 0.3 \text{ M Cl}^-$$

 \therefore

$$V_{\text{CaCl}_2} \times M_{\text{Cl}^-} = 2.5$$

$$V_{\text{CaCl}_2} = \frac{2.50 \text{ millimol}}{0.30 \text{ M}} = 8.3 \text{ mL CaCl}_2.$$

$$\text{Volume of the final solution} = 25 + 8.3 = 33.3 \text{ mL}$$

$$\text{Moles of Ca}^{2+} \text{ added} = 0.15 \text{ M} \times \frac{8.3}{1000} \text{ litre}$$

$$\text{Concentration of Ca}^{2+} = 0.15 \times \frac{8.3}{1000} \times \frac{1000}{33.3} = 0.037 \text{ M Ca}^{2+}$$

$$\text{Moles of NO}_3^- = \frac{0.1 \times 25}{1000} \text{ moles}$$

$$\text{Concentration of NO}_3^- = \frac{0.1 \times 25}{1000} \times \frac{1000}{33.3} = 0.075 \text{ M NO}_3^-$$

Problem 10. 20 mL of 0.25 M $\text{Al}_2(\text{SO}_4)_3$ is mixed with 40 mL of 0.30 M BaCl_2 . Barium sulphate precipitates out. What species are left in the final solution and what are their concentration ?



$$\begin{aligned} 20 \text{ mL of } 0.25 \text{ M Al}_2(\text{SO}_4)_3 &= 0.25 \text{ M} \times 20 \text{ mL Al}_2(\text{SO}_4)_3 \\ &= 5 \text{ millimoles Al}_2(\text{SO}_4)_3 \\ &= 2 \times 5 \text{ millimoles Al}^{3+} \\ &= 3 \times 5 = 15 \text{ millimoles SO}_4^{2-} \end{aligned}$$

$$\begin{aligned} 40 \text{ mL of } 0.30 \text{ M BaCl}_2 &= 0.30 \text{ M} \times 40 \text{ mL BaCl}_2 \\ &= 12 \text{ millimoles BaCl}_2 \\ &= 12 \text{ millimoles Ba}^{2+} \\ &= 2 \times 12 \text{ millimoles Cl}^- \end{aligned}$$

12 millimoles of Ba^{2+} react with 12 millimoles SO_4^{2-}

\therefore Millimoles of SO_4^{2-} left unreacted = $15 - 12 = 3$ millimoles

$$\text{Final volume of solution} = 20 + 40 = 60 \text{ mL}$$

$$\text{Concentration of SO}_4^{2-} = \frac{3}{1000} \times \frac{1000}{60} = 0.05 \text{ M SO}_4^{2-}$$

$$\text{Concentration of Cl}^- = \frac{2 \times 12}{1000} \times \frac{1000}{60} = 0.4 \text{ M Cl}^-$$

$$\text{Concentration of Al}^{3+} = \frac{2 \times 5}{1000} \times \frac{1000}{60} = 0.17 \text{ M Al}^{3+}.$$

Problem 11. A coin weighing 0.25 g was dissolved in excess conc. HNO_3 and oxides of nitrogen expelled by boiling. The solution was diluted with 25 mL water. This solution requires 45.5 mL of potassium thiocyanate solution (0.4 g of KCNS per 100 mL) for complete precipitation of silver. What is the percentage of silver in the coin? ($\text{Ag} = 108 \text{ amu}$).

$$\begin{aligned} \text{Solution. Equivalent mass of KCNS} &= \frac{\text{Molecular mass of KCNS}}{1} \\ &= 39 + 12 + 14 + 32 = 97 \text{ g/equiv} \end{aligned}$$



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$$\frac{137 + 2 \times 127}{2} = \frac{391}{2} = 195.5 \text{ g/equiv.}$$

$$\text{Let mass of BaI}_2 = x \text{ g}$$

$$\text{Mass of LiCl} = (0.6 - x) \text{ g}$$

$$\text{Equivalents of BaI}_2 = \frac{x}{195.5}$$

$$\text{Equivalents of LiCl} = \frac{0.6 - x}{42.5}$$

$$\text{Milli-equivalents of AgNO}_3 \text{ added} = 0.2 \text{ N} \times 40.0 \text{ mL} = 8.0$$

$$\text{Milli-equivalents of KCNS required} = 0.1 \text{ N} \times 25 \text{ mL} = 2.5$$

$$\text{Milli-equivalents of AgNO}_3 \text{ used} = 8 - 2.5 = 5.5$$

$$5.5 \text{ Milli-equivalents} = \frac{5.5}{1000} \text{ equivalents}$$

$$\therefore \frac{x}{195.5} + \frac{0.6 - x}{42.5} = \frac{5.5}{1000}$$

$$42.5x + 195.5 \times 0.6 - 195.5x = \frac{5.5}{1000} \times 195.5 \times 42.5$$

$$42.5x + 117.3 - 195.5x = 45.7$$

$$153x = 71.6$$

$$x = \frac{71.6}{153} \text{ g}$$

$$\text{Percentage of BaI}_2 = \frac{71.6 \text{ g}}{153} \times \frac{100}{0.6 \text{ g}}$$

$$\begin{array}{ccc} \text{BaI}_2 & = & 2\text{I} \\ 1 \text{ mol} & & 2 \text{ mol} \\ 391 \text{ g} & & 2 \times 127 \text{ g} \end{array}$$

$$\text{Percentage of I} = \frac{71.6}{153} \times \frac{100}{0.6} \times \frac{2 \times 127}{391} = 50.7\% \text{ I.}$$

Problem 14. A mixture of Na_2CO_3 and NaCl weighing 0.170 g was dissolved in water. The solution required 4.0 mL of 0.25 N HCl for complete neutralization. The resulting solution required 30 mL of 0.1 M AgNO_3 for complete precipitation of chloride. Calculate the percentages of Na_2CO_3 and NaCl in the mixture.



$$\begin{aligned} \text{Equivalent mass of Na}_2\text{CO}_3 &= \frac{\text{Molecular mass of Na}_2\text{CO}_3}{2} \\ &= \frac{106}{2} = 53 \text{ g/equiv.} \end{aligned}$$



$$\text{Equivalent mass of NaCl} = \text{Molecular mass of NaCl} = 58.5 \text{ amu}$$

$$\text{Equivalent mass of AgNO}_3 = \text{Molecular mass of AgNO}_3$$

$$N_{\text{AgNO}_3} = M_{\text{AgNO}_3}$$



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PROBLEMS FOR PRACTICE

1. How many grams of copper chips may be dissolved in 150 millilitres of 4 M HNO_3 ?

$$3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO}\uparrow + 4\text{H}_2\text{O}$$
2. (a) What volume of Cl_2 at STP will react with 35.0 mL of 1.5 M NaOH ?

$$3\text{Cl}_2 + 6\text{NaOH} \longrightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$$
 (b) What is the concentration of ClO_3^- ions in grams per litre after the reaction is complete?
3. $\text{FeS} + 2\text{HCl} \longrightarrow \text{H}_2\text{S} + \text{FeCl}_2$
 10.0 g powdered iron sulphide is dissolved in 50 mL of hydrochloric acid (density 1.19 g mL^{-1} containing 37% HCl by weight). After FeS is completely dissolved, the solution is diluted to 600 mL.
 (a) What is the molarity of free HCl in the resulting solution?
 (b) What are the concentrations of Fe^{2+} and Cl^- ions in the solution?
4. How many millilitres of HCl gas at STP will neutralize completely 40 millilitres of 0.80 N KOH solution? How many millimoles of KCl will be formed?
5. The weight of 0.378 equivalent M $(\text{OH})_2$ is 26.79 g. What is the atomic mass of M?
6. 2 mL of phosphoric acid (Sp. Gr. 1.70 containing 85.5% H_3PO_4 by weight) is added to 100 mL 0.6, 0.7 N NaOH .
 (a) How many grams of which reagent will remain unneutralized?
 (b) How many grams of Na_3PO_4 will be formed? ($\text{P} = 31 \text{ amu}$)
7. $2\text{Al} + 3\text{Zn}(\text{NO}_3)_2 \longrightarrow 2\text{Al}(\text{NO}_3)_3 + 3\text{Zn}$
 How many grams of aluminium will react with 75.0 mL of 0.2 M $\text{Zn}(\text{NO}_3)_2$? ($\text{Al} = 27$; $\text{Zn} = 65.5$)
8. $\text{Fe} + 2\text{AgNO}_3(\text{aq}) \longrightarrow 2\text{Ag} + \text{Fe}(\text{NO}_3)_2$
 How many millilitres of 0.25 N AgNO_3 will react with 0.2 g iron? ($\text{Fe} = 56$).
9. $\text{Zn} + \text{CuSO}_4 \longrightarrow \text{ZnSO}_4 + \text{Cu}$
 A zinc rod was kept in 85 ml of a copper sulphate solution. After a certain interval of time zinc displaced Cu^{2+} completely and the mass of copper deposited was 0.1534 g. What was the molarity of the CuSO_4 solution?
10. A solution is 0.25 M Na_2SO_4 .
 (a) How many millimoles Na_2SO_4 are in 15 mL solution?
 (b) How many millimoles SO_4^{2-} are in 20 mL solution?
 (c) How many grams S is present in 5 mL solution?
11. 70 millilitres of 4.0 M KNO_3 solution is mixed with 50 millilitres of a 3.0 M HCl solution? What are the final concentrations of KNO_3 and HCl in the mixture?
12. How many millilitres of a 0.4 M solution of $\text{Ba}(\text{NO}_3)_2$ will react with 80 mL of 0.4 M solution of Na_3PO_4 ?
13. $2\text{FeCl}_3 + 3\text{Ag}_2\text{SO}_4 \longrightarrow 6\text{AgCl}\downarrow + \text{Fe}_2(\text{SO}_4)_3$
 How many millilitres of 1.2 N Ag_2SO_4 will react with 22 millilitres of 0.5 M FeCl_3 ?
14. In the analysis of bromide by Mohr method, how many millilitres of 0.05 N AgNO_3 are required for completely precipitating bromide in 15.6 millilitres of 0.02 M BaBr_2 ?



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Structure of Atom

- 1. Atom.** It is made up of two parts. Its central portion known as nucleus contains protons and neutrons and is positively charged. The extra-nuclear part contains electrons and is negatively charged.
- 2. Atomic-number of an element.** It is equal to the number of protons in the nucleus of an atom of the element.

$$\begin{aligned}\text{Atomic-number (Z)} &= \text{Number of protons in the nucleus of an atom} \\ &= \text{Number of electrons in the extra-nuclear part of a neutral atom.}\end{aligned}$$

- 3. Mass-number of an element.** It is equal to the sum of the number of protons and neutrons in an atom of an element.

$$\begin{aligned}\text{Mass-number (A)} &= \text{Number of protons} + \text{Number of neutrons} \\ \text{Number of neutrons} &= A - Z\end{aligned}$$

- 4.** A_ZX is the symbol of an element. Z is its atomic-number and A is its mass-number.
- 5. Isotopes.** These are the atoms of the same element having same number of protons and electrons but different number of neutrons, e.g. ${}^{35}_{17}\text{Cl}$, ${}^{37}_{17}\text{Cl}$.
- 6. Isobars.** These are the atoms of the different elements having the same mass-numbers, e.g., ${}^{40}_{20}\text{Ca}$, ${}^{40}_{18}\text{Ar}$.
- 7. Isotones.** These are the atoms of different elements having the same numbers of neutrons, e.g., ${}^{30}_{14}\text{Si}$, ${}^{31}_{15}\text{P}$.
- 8. Nucleons.** It is a term used to represent the sum of protons and neutrons in the nucleus of an atom.
- 9. Atomic-mass of an element.** Most elements occur in nature as mixture of isotopes. Their percentage abundances are different and so the atomic-mass of an element is the weighted average of the atomic-masses of the natural isotopes.

$$(i) \quad \text{Fractional-abundance} = \text{Percentage-abundance} \times \frac{1}{100}$$

$$(ii) \quad \text{Atomic-mass} = \sum \text{Fractional-abundance} \times \text{Mass}$$

- 10.** $Q = ne^-$

where,

e^- = charge on an electron or proton

n = number of electrons or protons

Q = total charge



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Number of unit positive charges on $\text{Fe}^{3+} = 3$

$$\begin{aligned}\therefore \text{Charge in coulombs on } \text{Fe}^{3+} &= 3 \times 1.60 \times 10^{-19} \\ &= 4.80 \times 10^{-19} \text{ coulomb}\end{aligned}$$

AVERAGE ATOMIC-MASS AND ISOTOPES

Problem 6. A naturally occurring mixture of chlorine has the following fractional-abundances of its isotopes : $^{35}_{17}\text{Cl}$ (0.7553) and $^{37}_{17}\text{Cl}$ (0.2447). The atomic-masses of ^{35}Cl and ^{37}Cl are 34.97 and 36.95 amu respectively. What is the atomic-mass of chlorine?

$$\begin{aligned}\text{Solution. Atomic-mass} &= \Sigma \text{ Fractional-abundance} \times \text{Mass} \\ &= \text{F. Abundance of } ^{35}\text{Cl} \times \text{Mass } ^{35}\text{Cl} \\ &\quad + \text{F. Abundance of } ^{37}\text{Cl} \times \text{Mass } ^{37}\text{Cl} \\ &= 0.7553 \times 34.97 + 0.2447 \times 36.95 \\ &= 26.41 + 9.04 = 35.45 \text{ amu.}\end{aligned}$$

Problem 7. The element silver consists of two isotopes $^{107}_{47}\text{Ag}$ with a mass of 106.906 amu and $^{109}_{47}\text{Ag}$ with a mass of 108.95 amu. What is the percent-abundance of each of the two isotopes if the atomic mass of silver is 107.868 ?

Solution. Let x be the abundance of $^{107}_{47}\text{Ag}$ then abundance of $^{109}_{47}\text{Ag}$ is $(1 - x)$

$$\begin{aligned}\text{Atomic-mas} &= \Sigma \text{ Fractional-abundance} \times \text{Mass} \\ 107.868 &= x \times 106.906 + (1 - x) \times 108.95 \\ &= 106.906x + 108.95 - 108.95x \\ \text{or } 2.044x &= 1.082 \\ x &= \frac{1.082}{2.044} = 0.5294\end{aligned}$$

$$\therefore \text{Fractional-abundance of } ^{109}_{47}\text{Ag} = 0.5294$$

$$\text{or Percentage-abundance of } ^{107}_{47}\text{Ag} = 0.5294 \times 100 = 52.94\%$$

$$\text{Fractional-abundance of } ^{109}_{47}\text{Ag} = 1 - 0.5294 = 0.4706$$

$$\text{Percentage-abundance of } ^{109}_{47}\text{Ag} = 0.4706 \times 100 = 47.06\%$$

Problem 8. A sample of strontium is found to consist of three isotopes: ^{86}Sr , natural abundance 9.86%, ^{87}Sr , natural abundance 7.58% and ^{88}Sr , natural abundance 82.56%. Their relative atomic masses are 85.91, 86.91 and 87.91 respectively. Find the atomic-mass of strontium.

$$\begin{aligned}\text{Solution. Atomic-mass} &= \Sigma \text{ Fractional-abundance} \times \text{Mass} \\ \text{Atomic-mass Sr} &= (\text{F. abundance } ^{86}\text{Sr} \times \text{Mass } ^{86}\text{Sr}) + \\ &\quad (\text{F. abundance } ^{87}\text{Sr} \times \text{Mass } ^{87}\text{Sr}) + \\ &\quad (\text{F. abundance } ^{88}\text{Sr} \times \text{Mass } ^{88}\text{Sr})\end{aligned}$$



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Quantum-Mechanics

1. Light is a unique form of energy (electromagnetic-radiation) that travels through space at a constant velocity of $3.0 \times 10^8 \text{ m sec}^{-1}$.
2. The wavelength (λ) or frequency (ν) of an electromagnetic radiation is given by

$$c = \lambda \nu$$

where c is the velocity of light.

3. Planck's l.w. Light energy occurs as quanta called *photons*. The energy of one quanta or photon of an electromagnetic radiation is given by the Planck's law :

$$E = h \nu$$

where, E = energy in joules

ν = frequency in cycles per second

h = Planck's constant $6.626 \times 10^{-34} \text{ J-sec}$.

A body emits or absorbs energy in some definite whole number multiple amount known as quanta. Or radiations are emitted or absorbed discontinuously and not continuously.

4. Wave-number. It is the reciprocal of wavelength (λ).

$$\bar{\nu} = \frac{1}{\lambda}$$

5. Kinetic-energy of an electron.

$$E = \frac{1}{2} m V^2$$

where, E is energy in joules

m is mass in kilogram

V is velocity in m sec^{-1} .

6. Energy of an electron. The energy of an electron in an orbit of Bohr atom or a single electron cation is given by

$$E = -\frac{Z e^2}{2r}$$

where, Z is atomic number

e is electron charge

r is radius of the orbit.

7. Bohr's theory of hydrogen atom. This theory states that only those orbits in which the angular momentum of an electron is an integral multiple of $h/2\pi$ actually exist in an atom.

$$mVr = \frac{nh}{2\pi}$$

- where, m = mass of the electron
 V = velocity of the electron
 r = radius of the orbit
 n = an integer 1, 2, 3...

8. The energy of an electron in an allowed energy level is given by the following expression :

$$E_n = -\frac{2\pi^2 Z^2 me^4}{n^2 h^2}$$

- where, $n = 1, 2, 3...$
 E is the energy of the electron in the n th orbit
 Z is the nuclear charge
 e is the charge on the electron
 m is the mass of the electron
 h is Planck's constant.

For a hydrogen atom, the energy associated with an orbit fits the equation :

$$E_n = \frac{E_1}{n^2} = \frac{-21.73 \times 10^{-19} \text{ J/atom}}{n^2}$$

where E_1 is the energy associated with the most stable orbit of a hydrogen atom (nearest to the nucleus with n equal to 1).

9. According to Bohr-model, the radius of an allowed orbit in a hydrogen atom or a cation with one electron and a nuclear charge Z is given by the relation:

$$r = \frac{n^2 h^2}{4 \pi^2 m e^2 Z}$$

The radius of an allowed orbit is also given by the following equation :

$$r_n = n^2 r_1$$

where r_n is the radius of the orbit with quantum number n and r_1 is the radius of the smallest allowed orbit with $n = 1$.

10. For hydrogen atom.

$$r_n = n^2 \times 0.053 \text{ nm}$$

$$r_1 = 0.053 \text{ nm}$$

11. **Balmer's law.** The wave-number and wave-length of a line in the emission-spectrum of hydrogen or one electron cation of nuclear charge Z is given by the following equation :

$$\bar{\nu} = \frac{1}{\lambda} = \frac{2\pi^2 Z^2 m e^4}{h^3 c} \left[\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right]$$

For hydrogen with nuclear charge, Z , equal to one,

$$\frac{1}{\lambda} = \frac{2\pi^2 m e^4}{h^3 c} \left[\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right]$$

$$= R_H \left[\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right]$$

where R_H is a constant known as Rydberg-constant. For hydrogen,

$$R_H = \frac{2\pi^2 m e^4}{h^3 c} = 10,973,731 \text{ m}^{-1}$$

n_{low} and n_{high} are two quantum-numbers, n_{high} being the larger of the two.

- 12. Frequency of a line in a line-spectra.** The frequency of a line in the emission-spectrum of hydrogen or one electron cation with nuclear charge Z is given by the equation

$$\nu = \frac{c}{\lambda} = \frac{2\pi^2 Z^3 m e^4}{h^3} \left[\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right]$$

For hydrogen atom, $\nu = \frac{c}{\lambda} = 3.289 \times 10^{15} \text{ sec}^{-1} \left[\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right]$

- 13.** $1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$
 $1 \text{ nm} = 10^{-7} \text{ cm} = 10^{-9} \text{ m}$
 $1 \text{ \AA} = 0.1 \text{ nm}$ and $1 \text{ nm} = 10 \text{ \AA}$

- 14.** $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
 $1 \text{ J} = 10^7 \text{ erg}$

- 15. Bohr-model and line-spectrum of hydrogen.** It consists of the following series of lines : Lyman, Balmer, Paschen, Brackett and Pfund series after which the continuous spectrum starts. The frequency of each line is given by the relation :

$$\nu = 3.289 \times 10^{15} \left[\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right] \text{ sec}^{-1}$$

- (a) Lyman-series, $n_{\text{low}} = 1$ and $n_{\text{high}} = 2, 3, 4, 5 \dots$
 (b) Balmer-series, $n_{\text{low}} = 2$ and $n_{\text{high}} = 3, 4, 5, 6 \dots$
 (c) Paschen-series, $n_{\text{low}} = 3$ and $n_{\text{high}} = 4, 5, 6 \dots$
 (d) Brackett-series, $n_{\text{low}} = 4$ and $n_{\text{high}} = 5, 6 \dots$
 (e) Pfund-series, $n_{\text{low}} = 5$ and $n_{\text{high}} = 6, 7 \dots$

- 16. Size of the nucleus.** The size of the atomic-nucleus can be calculated using the following equation :

$$\text{Radius } (r) \text{ of the atomic nucleus} = (1.3 \times 10^{-13}) m^{1/3}$$

where m is the mass number of the atom.

- 17. Density of the nucleus.**

$$d = \frac{\text{Mass of nucleus}}{\text{Volume of nucleus}} = \frac{\text{Mass number}}{\text{Avogadro's number}} \times \frac{1}{\frac{4}{3} \pi r^3}$$

where, r is the radius of the nucleus.

- 18. Theory of relativity and velocity of the particle.** The mass of a particle at high speed is given by the following relation :



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$$\text{or} \quad \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m sec}^{-1}}{1.00 \times 10^{15} \text{ sec}^{-1}} = 3.00 \times 10^{-7} \text{ m}$$

Problem 3. What is the number of photons of light with a wavelength of 4000 Å that provide 1 joule of energy?

$$\begin{aligned} \text{Solution} \quad E_{\text{photon}} &= h\nu = \frac{hc}{\lambda} \\ &= \frac{6.625 \times 10^{-34} \text{ J.s} \times 3.00 \times 10^8 \text{ m/s}}{4000 \times 10^{-10} \text{ m}} = 4.9687 \times 10^{-19} \text{ J} \end{aligned}$$

Number of photons that provide 1 joule of energy

$$= \frac{1.00}{4.9687 \times 10^{-19}} = 2.012 \times 10^{18} \text{ photons.}$$

Problem 4. A major visible line in an atomic emission spectrum occurs at 450 nm. How much does the energy of an electron decrease as this photon is emitted? $h = 6.626 \times 10^{-34} \text{ J-sec.}$

$$\begin{aligned} \text{Solution.} \quad E &= h\nu = h \frac{c}{\lambda} \\ &= \frac{(6.626 \times 10^{-34} \text{ J-sec}) \times (3.0 \times 10^8 \text{ m sec}^{-1})}{450 \times 10^{-9} \text{ m}} \\ &= 4.417 \times 10^{-19} \text{ J} \end{aligned}$$

Problem 5. The energy required to melt 1.00 g of ice is 333 J. Find the number of quanta of infrared radiation of frequency $4.67 \times 10^{13} \text{ s}^{-1}$ that must be absorbed in order to melt 0.5 g of ice.

$$\begin{aligned} \text{Solution.} \quad E &= h\nu \\ &= 6.626 \times 10^{-34} \text{ J-sec} \times 4.67 \times 10^{13} \text{ s}^{-1} = 30.9434 \times 10^{-21} \text{ J} \end{aligned}$$

\therefore One quanta of infrared-radiation provides $30.9434 \times 10^{-21} \text{ J}$ of energy.

$$\text{Energy required to melt 0.5 g. of ice} = \frac{0.5 \text{ g}}{1.0 \text{ g}} \times 333 \text{ J} = 166.5 \text{ J}$$

$$\therefore \text{ Number of quanta} = \frac{166.5 \text{ J}}{30.9434 \times 10^{-21} \text{ J}} = 5.38 \times 10^{21}$$

BOHR-MODEL

Problem 6. The radius of the first orbit in a hydrogen atom is 0.53 Å. What is the energy of the electron in this orbit?

$$\begin{aligned} \text{Solution.} \quad E_1 &= \frac{-Ze^2}{2r_1} = \frac{-1 \times (4.8 \times 10^{-10} \text{ esu})^2}{2 \times (0.53 \times 10^{-8} \text{ cm})} \\ &= -21.73 \times 10^{-12} \text{ erg/atom} \end{aligned}$$

Problem 7. Calculate the angular momentum of an electron in the orbit of the Bohr hydrogen atom that corresponds to the second excited state.

$$\text{Solution. Angular momentum} = mvr = \frac{nh}{2\pi}$$



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$$E_1 = \frac{-2 \times (3.143)^2 \times 1^2 \times (9.109 \times 10^{-28} \text{ g}) \times (4.8 \times 10^{-10} \text{ esu})^4}{1^2 \times (6.626 \times 10^{-27} \text{ erg-sec})^2}$$

$$= -21.73 \times 10^{-12} \text{ erg/atom.}$$

In SI units $E_n = \frac{-2 \pi^2 Z^2 m e^4}{k^2 n^2 h^2} = \frac{-Z^2 m e^4}{8 \epsilon_0^2 n^2 h^2}$

where $k = 4\pi \epsilon_0$ and ϵ_0 is the permittivity of free space (vacuum) and is a constant ($8.85 \times 10^{-12} \text{ J}^{-1} \text{ coul}^2 \text{ m}^{-1}$).

$$E_1 = \frac{-1^2 \times (9.109 \times 10^{-31} \text{ kg}) \times (1.6 \times 10^{-19} \text{ coul})^4}{8 \times (8.85 \times 10^{-12} \text{ J}^{-1} \text{ coul}^2 \text{ m}^{-1})^2 \times 1^2 \times (6.626 \times 10^{-34} \text{ J-sec})^2}$$

$$= -21.73 \times 10^{-19} \text{ J/atom}$$

$$= \frac{-21.73 \times 10^{-19}}{1.602 \times 10^{-19}} = -13.56 \text{ eV/atom.}$$

Problem 12. Calculate the radius of Bohr's first orbit for hydrogen atom.

Solution. $r_n = \frac{n^2 h^2}{4\pi^2 m e^2 Z}$

$$= \frac{1^2 \times (6.626 \times 10^{-27} \text{ erg-sec})^2}{4 \times (3.143)^2 \times (9.109 \times 10^{-28} \text{ g}) \times (4.8 \times 10^{-10} \text{ esu})^2 \times 1}$$

$$= 0.53 \times 10^{-8} \text{ cm}$$

$$= 0.54 \times 10^{-8} \times 10^8 = 0.53 \text{ \AA}$$

In SI units

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2 Z}$$

$$= \frac{4\pi \epsilon_0 n^2 h^2}{4\pi^2 m e^2 Z} = \frac{\epsilon_0 n^2 h^2}{\pi m e^2 Z}$$

$$r_1 = \frac{(8.85 \times 10^{-12} \text{ J}^{-1} \text{ coul}^2 \text{ m}^{-1}) \times 1^2 \times (6.626 \times 10^{-34} \text{ J-sec})^2}{3.143 \times (9.109 \times 10^{-31} \text{ kg}) \times (1.6 \times 10^{-19} \text{ coul})^2 \times 1}$$

$$= 5.3 \times 10^{-11} \text{ m}$$

$$= 5.3 \times 10^{-11} \times 10^9 = 0.053 \text{ nm.}$$

Problem 13. Calculate the ionization-energy of hydrogen atom when the electron is removed from the first orbit to infinity.

Solution.

$$E_\infty - E_1 = \frac{-2\pi^2 Z^2 m e^4}{n_\infty^2 h^2} - \left[\frac{-2\pi^2 Z^2 m e^4}{n_1^2 h^2} \right]$$

$$= \frac{2\pi^2 Z^2 m e^4}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_\infty^2} \right]$$



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Solution.

$$E_3 = -2.41 \times 10^{-12} \text{ erg}$$

$$E_2 = -5.42 \times 10^{-12} \text{ erg}$$

$$\Delta E = E_3 - E_2$$

$$= -2.41 \times 10^{-12} \text{ erg} - (-5.42 \times 10^{-12} \text{ erg})$$

$$= -2.41 \times 10^{-12} \text{ erg} + 5.42 \times 10^{-12} \text{ erg}$$

$$= 3.01 \times 10^{-12} \text{ erg}$$

$$\Delta E = h\nu$$

or $\nu = \frac{\Delta E}{h} = \frac{3.01 \times 10^{-12} \text{ erg}}{6.62 \times 10^{-27} \text{ erg-sec}} = \frac{3.01}{6.62} \times 10^{15} \text{ sec}^{-1}$

As $c = \nu\lambda$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{10} \text{ cm sec}^{-1}}{\frac{3.01}{6.62} \times 10^{15} \text{ sec}^{-1}}$$

$$= \frac{3.00 \times 6.62 \times 10^{-5} \text{ cm}}{3.01} = 6.598 \times 10^{-5} \text{ cm.}$$

Problem 18. The electron energy in hydrogen atom is given by $E = (-21.7 \times 10^{-12})/n^2$ ergs. Calculate the energy required to remove an electron completely from the $n=2$ orbit. What is the longest wavelength in (cm) of light that can be used to cause this transition? (IIT/JEE 1984)

Solution.

$$E_2 = \frac{(-21.7 \times 10^{-12})}{n^2} \text{ erg}$$

$$E_\infty = \frac{-21.7 \times 10^{-12}}{\infty^2} \text{ erg}$$

$$\Delta E = E - E_2$$

$$= 21.7 \times 10^{-12} \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) = 21.7 \times 10^{-12} \left(\frac{1}{4} - 0 \right)$$

$$= 21.7 \times 10^{-12} \times \frac{1}{4} = 5.42 \times 10^{-12} \text{ erg}$$

Now, $\Delta E = h\nu = h \frac{c}{\lambda}$

or $\lambda = \frac{hc}{\Delta E} = \frac{6.625 \times 10^{-27} \text{ erg-sec} \times 3.0 \times 10^{10} \text{ cm sec}^{-1}}{5.42 \times 10^{-12} \text{ erg}}$

$$= 3.7 \times 10^{-5} \text{ cm.}$$

Problem 19. Calculate the wavelength in Angstroms of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionization-potential of the ground state of hydrogen atom is 2.17×10^{-11} erg per atom. (IIT/JEE 1984)

Solution. The energy of an electron at distance ∞ from the nucleus is zero. Therefore, ionization-potential of the ground state of hydrogen atom ($n = 1$) is, in fact, the energy of the electron in that orbit, with the sign reversed.



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$$\begin{aligned} \bar{\nu} &= \frac{1}{\lambda} = R_H \left(\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right) \\ \frac{1}{\lambda R_H} &= \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \\ \frac{1}{(10936 \times 10^{-9} \text{ m}) \times 1.0973 \times 10^7 \text{ m}^{-1}} &= \frac{1}{3^2} - \frac{1}{n_{\text{high}}^2} \\ \frac{1}{n_{\text{high}}^2} &= \frac{1}{9} - \frac{1}{12^2} = \frac{1}{36} \\ n_{\text{high}}^2 &= 36 \\ n_{\text{high}} &= \sqrt{36} = 6 \end{aligned}$$

Problem 22. The energy associated with an orbit in the hydrogen atom is given by the following equation $E_n = \frac{-13.6}{n^2} \text{ eV}$. What is the energy associated with the orbit having a radius of $16 r_1$, where r_1 is the radius of the first orbit?

Solution.

$$\begin{aligned} r_n &= n^2 r_1 \\ 16 r_1 &= n^2 r_1 \\ 4 &= n \\ E_n &= \frac{-13.6}{n^2} = \frac{-13.6}{4^2} = \frac{-13.6}{16} = -0.85 \text{ eV.} \end{aligned}$$

Problem 23. The ionization energy of hydrogen atom in ground state is 1312 kJ mol^{-1} . Calculate the wavelength of radiation emitted when the electron in this atom makes a transition from $n = 2$ state to $n = 1$ state. (Planck's constant, $h = 6.63 \times 10^{-34} \text{ J-s}$, velocity of light, $c = 3 \times 10^{10} \text{ cm s}^{-1}$ and Avogadro's number, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$).
(CBSE 2000)

Solution. The energy of the electron in the first orbit = -1312 kJ/mol

Energy of the electron in the second orbit = $\frac{-E_1}{n^2} = \frac{-1312}{2^2} \text{ kJ/mol} = \frac{-1312}{4} \text{ kJ/mol}$

$$\begin{aligned} \Delta E &= E_2 - E_1 = \frac{-1312}{4} - (-1312) = 1312 \times \frac{3}{4} \text{ kJ/mol} \\ &= 1312 \times \frac{3}{4} \times \frac{1}{6.02 \times 10^{23}} \text{ kJ/atom} \\ &= 163.5 \times 10^{-23} \text{ kJ/atom} = 163.5 \times 10^{-20} \text{ J/atom} \end{aligned}$$

$$\begin{aligned} \Delta E &= h\nu = \frac{hc}{\lambda} \\ \lambda &= \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \text{ J-s} \times 3 \times 10^8 \text{ ms}^{-1}}{163.5 \times 10^{-20} \text{ J/atom}} = 1.217 \times 10^{-7} \text{ m} \end{aligned}$$

Problem 24. The quantised energy of electron in hydrogen atom for the n th energy level is given by $E_n = -\frac{13.12}{n^2} \times 10^5 \text{ J mol}^{-1}$. Calculate the minimum energy required to



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Problem 27. The ionisation energy of H atom is 13.6 eV. What will be ionisation energy of He^+ and Li^{+2} ions ? (Roorkee 1986)

Solution. E_1 for $\text{He}^+ = E_1$ for H $\times Z^2 = 13.6 \times 4 = 54.4$ eV
 E_1 for $\text{Li}^{+2} = E_1$ for H $\times Z^2 = 13.6 \times 9 = 122.4$ eV

Problem 28. Calculate the velocity (cm/sec) of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolution per second that this electron makes around the nucleus. (Roorkee 1987)

Solution. (a) $m V_n r = \frac{nh}{2\pi}$
 $V_n = \frac{nh}{2\pi m r} = \frac{nh}{2\pi m (n^2 h^2 / 4\pi^2 m e^2 Z)} = \frac{2\pi e^2 Z}{nh}$
 $V_3 = \frac{2 \times 3.143 \times (4.8 \times 10^{-10} \text{ esu})^2 \times 1}{3 \times 6.63 \times 10^{-27} \text{ erg. sec}}$
 $= 7.28 \times 10^7 \text{ cm/sec.}$

Number of revolutions that an electron makes around the nucleus

$$= \frac{\text{Velocity of electron}}{\text{Circumference of the orbit}}$$

$$= \frac{V_n}{2\pi r_n} = \frac{nh}{2\pi m r_n (2\pi r_n)} = \frac{nh}{4\pi^2 m r_n^2}$$

$$= \frac{nh}{4\pi^2 m (n^2 h^2 / 4\pi^2 m e^2 Z)^2} = \frac{4\pi^2 m e^4 Z^2}{n^3 h^3}$$

$$= \frac{4 \times (3.143)^2 \times 9.1 \times 10^{-28} \text{ g} \times (4.8 \times 10^{-10} \text{ esu})^4 \times 1^2}{3^3 \times (6.63 \times 10^{-27} \text{ erg. sec})^3}$$

$$= 2.42 \times 10^{14} \text{ revolutions per second.}$$

Problem 29. Arrange the orbitals represented by the following sets of energy :

- (i) $n = 4, l = 0, m_l = 0, m_s = +1/2$
- (ii) $n = 3, l = 1, m_l = 1, m_s = -1/2$
- (iii) $n = 3, l = 2, m_l = 0, m_s = +1/2$
- (iv) $n = 3, l = 0, m_l = 0, m_s = -1/2$

(Roorkee 1987)

Solution. The given set of quantum numbers represent the following orbitals : (i) 4s (ii) 3p (iii) 3d (iv) 3s. The decreasing order of energy of these orbitals is

$$(iii) > (i) > (ii) > (iv)$$

$$3d > 4s > 3p > 3s$$

Problem 30. Calculate the wavelength and energy of radiation emitted for the electronic transition from infinity (∞) to stationary state one of the hydrogen atom. (Roorkee 1988)

Solution. $\frac{1}{\lambda} = R_H \left(\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right)$
 $= R_H \left(\frac{1}{1^2} - \frac{1}{\infty} \right) = R_H$



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$$\begin{aligned}
 &= 1.09677 \times 10^7 \text{ m}^{-1} \times 1^2 \times 6.626 \times 10^{-34} \text{ J-s} \times 3 \times 10^8 \text{ ms}^{-1} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \\
 &= 1.09677 \times 10^7 \times 6.626 \times 10^{-34} \times 3 \times 10^8 \times \frac{3}{4} \\
 &= 1.635 \times 10^{-18} \text{ J} \\
 \frac{1}{\lambda} &= R_H Z^2 \left(\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right) \\
 \frac{1}{3 \times 10^{-8} \text{ m}} &= 1.0967 \times 10^7 \text{ m}^{-1} \times Z^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \\
 Z^2 &= \frac{1}{3 \times 10^{-8} \times 1.0967 \times 10^7} \times \frac{4}{3} = 4 \\
 Z &= 2
 \end{aligned}$$

This atomic number correspond to He^+ .

Problem 38. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of the spectrum? (IIT/JEE 1993)

Solution. (a)

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\therefore R_H Z_1^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R_H Z_2^2 \left(\frac{1}{n_1^2(\text{H}_2)} - \frac{1}{n_2^2(\text{H}_2)} \right)$$

For He^+ , $Z_1 = 2$ For H^+ , $Z_2 = 1$

$$\therefore 1 \left(\frac{1}{n_1^2(\text{H}_2)} - \frac{1}{n_2^2(\text{H}_2)} \right) = 2^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{n_1^2(\text{H}_2)} - \frac{1}{n_2^2(\text{H}_2)} = 4 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = 4 \times \frac{3}{16} = \frac{3}{4}$$

When $n_1(\text{H}_2) = 1$ and $n_2(\text{H}_2) = 2$

$$\frac{1}{n_1^2(\text{H}_2)} - \frac{1}{n_2^2(\text{H}_2)} = \frac{1}{1^2} - \frac{1}{2^2} = \frac{3}{4}$$

\therefore Transition from $n = 2$ to $n = 1$ in the hydrogen atom has the same wavelength as the Balmer transition from $n = 4$ to $n = 2$.

Problem 39. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms.

(Bond energy of $\text{I}_2 = 240 \text{ kJ mol}^{-1}$)

(IIT/JEE 1995)

Solution. (a) Bond energy of I_2 molecule $= 240 \text{ kJ mol}^{-1}$

$$\begin{aligned}
 &= \frac{240}{6.023 \times 10^{23}} \text{ kJ/molecule} \\
 &= 3.98 \times 10^{-22} \text{ kJ} = 3.98 \times 10^{-19} \text{ J}
 \end{aligned}$$



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PROBLEMS FOR PRACTICE

1. What is the frequency and energy of a photon of light whose wavelength is 590 nm? The Planck's constant, h , is 6.63×10^{-34} J-s.
2. What is the frequency and energy per quantum of an X-ray with a wavelength of 2.0×10^{-11} m? (h is 6.63×10^{-34} J-s.)
3. A hot object emits a photon having an energy of 4.0×10^{-21} J. What is the frequency of the emitted light? (h is 6.625×10^{-34} J-s.)
4. What is the wavelength of a radiowave with a frequency of 1200 kHz?
5. The bond-energy of a covalent bond between two atoms is 418 kJ mol^{-1} . What is the maximum wave-length that will cause the photo-dissociation of the bond?
6. Calculate and compare the energies of two radiations which have wavelengths 6000 Å and 4000 Å. (AISS 1982)
7. A gaseous mixture contains fluorine atoms and chlorine atoms. Removal of an electron from each atom of the sample requires a total of 284 kJ; addition of an electron to each atom of the assembly releases a total of 68.8 kJ. How many atoms of each kind are there in the original sample?
For F: $\text{IE} = 27.91 \times 10^{-22}$ kJ and $\text{EA} = 5.53 \times 10^{-22}$ kJ
For Cl: $\text{IE} = 20.77 \times 10^{-22}$ kJ and $\text{EA} = 5.78 \times 10^{-22}$ kJ
8. The radius of the third orbit in a hydrogen atom is 4.5 Å. What is the energy of the electron in this orbit?
9. Calculate the angular momentum of an electron-rotating in the fourth excited state in a Bohr atom. $h = 6.626 \times 10^{-34}$ J-sec.
10. An electron is moving with a velocity of $3.4 \times 10^6 \text{ m sec}^{-1}$. Calculate its energy in (i) joules and (ii) electron-volts.
11. The radius of the second orbit in a Bohr atom is 0.21 nm. What is the velocity of the electron in this orbit? $m_{\text{He}} = 9.11 \times 10^{-31}$ kg.
12. The radius of the second Bohr's orbit in He^+ cation is 1.06 Å. What is the velocity of the electron rotating in this orbit? $m_e = 9.11 \times 10^{-28}$ g and $e = 4.8 \times 10^{-10}$ esu.
13. Calculate the energy of an electron rotating in the second orbit of hydrogen atom. $h = 6.626 \times 10^{-27}$ erg-sec, $e = 4.8 \times 10^{-10}$ esu.
14. Calculate the energy of an electron rotating in the fifth orbit of hydrogen atom. $h = 6.626 \times 10^{-34}$ J-sec, $e = 1.6 \times 10^{-19}$ C, $\epsilon_0 = 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$.
15. Calculate the radius of Bohr's fourth orbit for hydrogen atom.
 $h = 6.626 \times 10^{-27}$ erg-sec
16. Calculate the radius of the most stable orbit in hydrogen atom. $e = 1.6 \times 10^{-19}$ C, $\epsilon_0 = 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$.
17. Calculate the energy released when an electron returns to second orbit from infinity in a hydrogen atom.
18. Calculate the frequency of light that will ionize sodium atoms. The ionization-potential of sodium is 5.119 eV.
19. Find the frequency of the shortest wavelength radiation that can be emitted by hydrogen.



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$$\text{or } m = \frac{h}{\lambda V} = \frac{6.62 \times 10^{-34} \text{ Js}}{1 \times 10^{-10} \text{ m} \times 6.0 \times 10^4 \text{ ms}^{-1}} \\ = 1.10 \times 10^{-28} \text{ kg}$$

Problem 7. Find the velocity of an electron whose wavelength is $2.0 \times 10^{-10} \text{ m}$. $h = 6.626 \times 10^{-34} \text{ J-sec}$.

$$\text{Solution. } \lambda = \frac{h}{mV} \\ \text{or } V = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34} \text{ J-sec}}{9.11 \times 10^{-31} \text{ kg} \times 2.0 \times 10^{-10} \text{ m}} \\ = 3.636 \times 10^6 \text{ m sec}^{-1}$$

Problem 8. Find the wavelength of a carbon dioxide molecule moving at a velocity of 440 m sec^{-1} .

$$\text{Solution. } \text{Molecular mass of CO}_2 = 12 + 2 \times 16 = 44 \text{ amu} \\ \text{Mass of a CO}_2 \text{ molecule} = \frac{M}{N} = \frac{44 \text{ g/mol}}{6.023 \times 10^{23} \text{ mol}^{-1}} \\ = \frac{44}{6.023 \times 10^{23} \times 1000} \text{ kg} \\ = 0.0073 \times 10^{-23} \text{ kg} \\ \lambda = \frac{h}{mV} = \frac{6.626 \times 10^{-34} \text{ J sec}}{0.0073 \times 10^{-23} \text{ kg} \times 440 \text{ m sec}^{-1}} \\ = 2.063 \times 10^{-11} \text{ m}$$

Problem 9. An electron is moving with a kinetic energy of $2.275 \times 10^{-25} \text{ J}$. Calculate its de-Broglie wavelength. Mass of electron is $9.1 \times 10^{-31} \text{ kg}$; $h = 6.6 \times 10^{-34} \text{ J-s}$.

(CBSE 1999 Comptt.)

$$\text{Solution. } \text{Kinetic energy} = \frac{1}{2} mV^2 = 2.275 \times 10^{-25} \text{ J} \\ V^2 = \text{K.E} \times \frac{2}{m} \\ = 2.275 \times 10^{-25} \text{ J} \times \frac{2}{9.1 \times 10^{-31} \text{ kg}} = 0.5 \times 10^6 \text{ m}^2 \\ V = \sqrt{0.5 \times 10^6 \text{ m}^2} = 0.7 \times 10^3 \text{ ms}^{-1} \\ \lambda = \frac{h}{mV} = \frac{6.6 \times 10^{-34} \text{ J-s}}{(9.1 \times 10^{-31} \text{ kg} \times 0.7 \times 10^3 \text{ ms}^{-1})} \\ = 1.036 \times 10^{-6} \text{ m}$$

Problem 10. Calculate the de-Broglie wavelength of an electron, travelling with a speed equal to 1% of the speed of light. $h = 6.626 \times 10^{-34} \text{ J-s}$, $m_e = 9.1 \times 10^{-31} \text{ kg}$, $c = 3 \times 10^8 \text{ ms}^{-1}$.

(CBSE 1994 Comptt.)

$$\text{Solution. } \text{Velocity of the electron, } V = 1\% \text{ of speed of light}$$



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PROBLEMS FOR PRACTICE

1. Calculate the uncertainty in position of a dust particle with a mass equal to 1 mg if the uncertainty in its velocity is $5.5 \times 10^{-20} \text{ ms}^{-1}$. h is $6.6 \times 10^{-34} \text{ J-s}$.
2. The approximate mass of an electron is 10^{-27} g . Calculate the uncertainty in its velocity if the uncertainty in its position were of the order of $\pm 10^{-11} \text{ m}$.
3. A base-ball of mass 200 g is moving with a velocity of $3.0 \times 10^2 \text{ cm s}^{-1}$. If we can locate the base-ball with an error equal in magnitude to the wavelength of the light used, 5000 Å, how will the uncertainty in momentum be compared with the total momentum of the base-ball?
4. Calculate the uncertainty in position of an electron if the uncertainty in the velocity is $5.7 \times 10^5 \text{ m/sec}$, $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$, mass of electron = $9.1 \times 10^{-28} \text{ g}$.
5. Calculate the wavelength associated with an electron wave (mass $9.1 \times 10^{-31} \text{ kg}$) moving with a velocity of 10^3 ms^{-1} .
(AISSC 1982, 79; DSSC 1985)
6. Calculate the momentum of a particle which has a de-Broglie wavelength of 1 Å.
(DSSC 1983, 80)
7. Calculate the wavelength of a 100 kg rocket moving with a velocity of 300 km per hour, $h = 6.6 \times 10^{-34} \text{ joule-sec}$.
8. What is the mass of a photon of sodium light with a wavelength of 5890 Å. The velocity of light, c , is $3.00 \times 10^{10} \text{ cm sec}^{-1}$ and Planck's constant, h , is $6.63 \times 10^{-27} \text{ erg-sec}$.
9. An electron is moving with a kinetic-energy of $4.55 \times 10^{-25} \text{ joule}$. Calculate its wavelength. Mass of an electron is $9.1 \times 10^{-31} \text{ kg}$ and Planck's constant is $6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$.
10. Calculate the momentum of a particle which has a de-Broglie wavelength of $2.5 \times 10^{-10} \text{ m}$. $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$.
(AISS 1984, 80)
11. Find the velocity of a neutron whose wavelength is 1000 nm. $m_n = 1.67 \times 10^{-27} \text{ kg}$.
12. Find the wavelength of a benzene molecule moving at a velocity of $6.0 \times 10^8 \text{ m s}^{-1}$.
13. When would the wavelength associated with an electron be equal to the wavelength associated with a proton. Mass of electron = $9.1095 \times 10^{-28} \text{ g}$, mass of proton = $1.6725 \times 10^{-24} \text{ g}$.
(CBSE 1990)
14. An electron has a speed of 40 ms^{-1} , accurate upto 99.99%. What is the uncertainty in locating its position? Mass of electron is $9.1 \times 10^{-31} \text{ kg}$.

Hint $\Delta V = \frac{100 - 99.99}{100} \times 40 \text{ ms}^{-1}$

(Punjab 1990)
15. The uncertainties in the position and velocity of a particle are 10^{-10} m and $5.27 \times 10^{-24} \text{ ms}^{-1}$. Calculate the mass of the particle. $h = 6.626 \times 10^{-34} \text{ J-s}$.
(CBSE 1989, Punjab 1991)
16. Calculate the uncertainty in momentum of an electron if it is confined to a linear region of length $1 \times 10^{-10} \text{ m}$.
Hint: $\Delta x = 1 \times 10^{-10} \text{ m}$.
(CBSE 1995 Comptt)



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(iii) **Actinium series.** It begins with ${}^{235}_{92}\text{U}$ and decay to ${}^{207}_{82}\text{Pb}$. It is also known as $4n + 3$ series.

($4n + 1$ series of radioactive elements is not known in nature). Each member of the series is in equilibrium with the very long lived parent nuclide.

5. Induced radioactivity. Conversion of stable nuclei into radioactive ones is called nuclear transmutation. It is brought about by bombarding the stable nuclei with highly accelerated particles like alpha, electron, neutron etc. The result of the bombardment is the formation of a new element with radioactive properties.

Rutherford was the first person to report the formation of a new element by nuclear transmutation. In 1911, he bombarded nitrogen gas with α -particles and obtained proton and oxygen :



In 1934, Irene Joliot Curie bombarded aluminium with α -particles from polonium.



6. Rate equation for the radioactive-decay. The number of atoms disintegrating per unit time of a radioactive sample does not depend in any way on :

(i) The state of the radioactive sample. *The activity is the same whether it is a metal or its chloride, hydroxide or any other compound.*

(ii) Temperature.

(iii) Applied pressure.

(iv) Electric, magnetic or gravitational fields.

All radioactive decay processes follow a first order rate law. The rate of radioactive decay at time t is directly proportional to the number of radioactive atoms present at time t .

$$-\frac{dN}{dt} \propto N$$

or $\ln \frac{N_0}{N} = kt$

or $2.303 \log \frac{N_0}{N} = kt$

$$t = \frac{2.303}{k} \log \frac{N_0}{N}$$

where, N_0 = Number of radioactive atoms at time $t = 0$.

N = Number of radioactive atoms at time $t = t$.

k = decay-constant or radioactive-constant or disintegration-constant.
(Earlier symbol λ was used)



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alpha particles are given out



(ii) ${}_{7}^{14}\text{N}$ (n, p). This indicates that when ${}_{7}^{14}\text{N}$ is bombarded with neutrons, protons are given out.



Problem 2. Write nuclear equations for the decay of



Problem 3. Write nuclear equations for



Problem 4. ${}_{90}^{234}\text{Th}$ disintegrates to give ${}_{82}^{206}\text{Pb}$ as the final product. How many alpha and beta particles are emitted during this process? (IIT/JEE 1986)



(a) Change in mass number = $234 - 206 = 28$

Emission of an α -particle decreases mass number by 4 units

$$\therefore \text{Number of } \alpha\text{-particles emitted} = \frac{28}{4} = 7$$

(b) Emission of an α -particle decreases atomic number by 2 units whereas emission of a beta particle increases atomic number by 1 unit.

Total decrease in atomic number by emission of 7-alpha particles = $2 \times 7 = 14$

As atomic number changes from 90 to 82, difference in atomic numbers is $90 - 82 = 8$.

$$\therefore \text{Number of beta particles emitted} = 14 - 8 = 6$$

Problem 5. What are the atomic number and mass number of the new element formed if three alpha and four beta particles are emitted by ${}_{92}^{235}\text{U}$?

Solution. Emission of 3- α -particles decreases mass number by $3 \times 4 = 12$ units

$$\therefore \text{Mass number of the new element} = 235 - 12 = 223.$$

Emission of 3 α -particles decreases atomic number by $3 \times 2 = 6$ units

Emission of 4-beta particles increases atomic number by $4 \times 1 = 4$ units.

$$\therefore \text{Net decrease in atomic number} = 6 - 4 = 2 \text{ units}$$

$$\therefore \text{Atomic-number of the new element} = 92 - 2 = 90$$

The new element is represented as ${}_{90}^{223}\text{X}$.



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$$\begin{aligned}
 N &= \frac{2.296 \times 10^{14} \times 80.3 \times 24 \times 60 \times 60}{0.693} \text{ atom} \\
 &= \frac{2.296 \times 10^{14} \times 80.3 \times 24 \times 60 \times 60 \text{ atom}}{0.693} \times \frac{73 \text{ g/mol}}{6.023 \times 10^{23} \text{ atom/mol}} \\
 &= 0.2784 \text{ g } ^{73}\text{As.}
 \end{aligned}$$

Problem 15. The half-life period of nickel-57 is 36.0 hour. What is its average life-period?

Solution. Average life-period $= \frac{1}{k} = \frac{t_{1/2}}{0.693} = 1.44 \times t_{1/2}$
 $= 1.44 \times 36.0 \text{ hour} = 51.84 \text{ hour.}$

Problem 16. $^{232}_{90}\text{Th}$ is an alpha particle emitter with a half-life of 1.41×10^{10} years. Given a 0.50 g sample of this thorium, how many alpha particles will it emit per second?

Solution. $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.41 \times 10^{10} \times 365 \times 24 \times 60 \times 60 \text{ sec}}$

Number of Th-232 atoms in 0.5 g N $= \frac{6.023 \times 10^{23} \text{ atom/mol} \times 0.5 \text{ g}}{232 \text{ g/mol}}$

No. of disintegrations per second $= \frac{-dN}{dt} = kN$

$$\begin{aligned}
 &= \frac{0.693 \times 6.023 \times 10^{23} \times 0.5}{1.41 \times 10^{10} \times 365 \times 24 \times 60 \times 60 \times 232} \\
 &= 2023 \text{ disintegrations sec}^{-1}
 \end{aligned}$$

As one Th-232 atom emits one alpha particle therefore number of alpha particles emitted per second = 2023.

Problem 17. A wooden article is found to have a ^{14}C to ^{12}C ratio that is 10% of the atmosphere. How old is the specimen? The half-life of ^{14}C is 5730 years.

Solution. Let relative number of $^{14}_6\text{C}$ atoms at ($t = 0$) is N_0

Relative number of $^{14}_6\text{C}$ atoms after t years $= N = \frac{10 N_0}{100} = 0.1 N_0$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} \text{ yr}^{-1}$$

$$\begin{aligned}
 t &= \frac{2.303}{k} \log \frac{N_0}{N} = \frac{2.303}{0.693} \times 5730 \text{ yr}^{-1} \log \frac{N_0}{0.1 N_0} \\
 &= \frac{2.303}{0.693} \times 5730 \times 1 = 19042.1 \text{ years.} \quad (\log 10 = 1)
 \end{aligned}$$

Problem 18. Radioactivity is a first order process. Radioactive carbon in a wood sample decays with a half-life of 5770 years. What is the rate-constant (in years^{-1}) for the decay? What fraction would remain after 11540 years? (IIT/JEE 1984)



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Problem 27. It is known that 1 g of ^{226}Ra emits 11.6×10^{17} alpha particles per year. Given the half-life of Ra^{226} be 1600 years. Compute the value of Avogadro's No.

(MLNR 1983)

Solution. \therefore Rate = $k N_0$

1 mole = 226 g Ra has Avogadro's No. atoms

\therefore 1 g Ra has = $\frac{\text{Av. No.}}{226}$ atoms = N_0

$$11.6 \times 10^{17} = \frac{0.693}{1600} \times \frac{\text{Av. No.}}{226}$$

\therefore Avogadro's No. = 6.052×10^{23}

Problem 28. With what velocity should an α -particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} metre from the nucleus of the copper atom?

(IIT/JEE 1997)

Solution. At closest distance of the α -particle kinetic energy of the α -particle should be equal to repulsion energy

$$\frac{1}{2} mu^2 = \frac{1}{4\pi\epsilon_0} \times \frac{2Ze^2}{r}$$

$$\therefore u^2 = \frac{Ze^2}{4\pi\epsilon_0 mr}$$

$$= \frac{29 \times (1.6 \times 10^{-19})^2}{3.14 \times 8.85 \times 10^{-12} \times (4 \times 1.672 \times 10^{-27}) \times 10^{-13}}$$

$$= 6.3 \times 10^6 \text{ m sec}^{-1}$$

Problem 29. Consider an α -particle just in contact with a $_{92}\text{U}^{238}$ nucleus. Calculate the coulombic repulsion energy (i.e., the height of coulombic barrier between U^{238} and α -particle) assuming that the distance between them is equal to the sum of their radii.

(MLNR 1996)

Solution. $r_{\text{nucleus}} = 1.3 \times 10^{-13} \times (A)^{1/3}$, Where A is mass number

$$r_{\text{U}^{238}} = 1.3 \times 10^{-13} \times (238)^{1/3} = 8.06 \times 10^{-13} \text{ cm}$$

$$r_{\text{He}^4} = 1.3 \times 10^{-13} \times (4)^{1/3} = 2.06 \times 10^{-13} \text{ cm}$$

\therefore Total distance in between uranium and α -nuclei

$$= 8.06 \times 10^{-13} + 2.06 \times 10^{-13} = 10.12 \times 10^{-13} \text{ cm}$$

Now repulsion energy = $\frac{Q_1 Q_2}{r}$

$$= \frac{92 \times 48 \times 10^{-10} \times 2 \times 48 \times 10^{-10}}{10.12 \times 10^{-13}} \text{ erg}$$

$$= 418.9 \times 10^{-7} \text{ erg}$$

$$= 418.9 \times 10^{-7} \times 6.242 \times 10^{11} \text{ eV}$$

$$= \frac{418.9 \times 10^{-7} \times 6.242 \times 10^{11}}{10^6} \text{ MeV} = 26.14 \text{ MeV.}$$



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$$\log \frac{N_0}{N_t} = \frac{kt}{2.303} = \frac{0.005 \text{ day}^{-1} \times 69.2 \text{ days}}{2.303} = 0.1502$$

$$\frac{N_0}{N_t} = \text{Antilog } 0.1502 = 1.414$$

$$N_t = \frac{N_0}{1.414} = \frac{1 \text{ g}}{1.414}$$

$$\text{Amount of Po decomposed} = 1 - \frac{1}{1.414} = \frac{0.414}{1.414} \text{ g}$$

$$\begin{aligned} \text{Moles of Po decomposed} &= \frac{\text{Mass of Po decomposed}}{\text{Atomic mass of Po}} \\ &= \frac{0.414 \text{ g}}{1.414 \times 210 \text{ g/mol}} \end{aligned}$$

1 Po atom emits 1 alpha particle which gets converted into 1 helium atom

\therefore 1 mol of Po emits 1 mole He gas

$$\frac{0.414}{1.414 \times 210} \text{ mol emits} = \frac{0.414}{1.414 \times 210} \text{ mol He gas}$$

1 mol of He gas occupies 22400 cm³ at STP

$$\begin{aligned} \frac{0.414}{1.414 \times 210} \text{ mol He gas occupies} &= \frac{0.414 \times 22400 \text{ cm}^3}{1.414 \times 210} \\ &= 31.23 \text{ cm}^3 \text{ He at STP} \end{aligned}$$

Problem 36. In nature a decay chain series starts with ${}_{90}\text{Th}^{232}$ and finally terminates at ${}_{82}\text{Pb}^{208}$. A thorium ore sample was found to contain 8×10^{-4} mL of helium at STP and 5×10^{-7} gm of Th^{232} . Find the age of the ore sample assuming the source of helium to be only due to the decay of Th^{232} . Also assume complete retention of helium within the ore. (Half-life of $\text{Th}^{232} = 1.39 \times 10^{10}$ Y). (Roorkee 1992)

Solution. 22,400 mL at STP = Avogadro number = 6.023×10^{23} atoms

$$\begin{aligned} 8 \times 10^{-4} \text{ mL of He at STP} &= \frac{6.023 \times 10^{23} \times 8 \times 10^{-4} \text{ mL}}{22400 \text{ mL}} \\ &= 2.15 \times 10^{15} \text{ atoms} \end{aligned}$$

When ${}_{90}^{232}\text{Th}$ decays to ${}_{82}^{208}\text{Pb}$, 6 alpha particles are given out.

\therefore Number of ${}_{90}^{232}\text{Th}$ atoms disintegrated

$$(N) = \frac{2.15 \times 10^{15}}{6} = 3.585 \times 10^{14} \text{ atoms}$$

Number of ${}_{90}^{232}\text{Th}$ atoms left (N_t) = 5×10^{-7} g

$$\begin{aligned} &= \frac{5 \times 10^{-7} \text{ g} \times 6.023 \times 10^{23}}{232 \text{ g mol}^{-1}} \\ &= 1.298 \times 10^{15} \text{ atoms} \end{aligned}$$



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Solution.

$$\text{Change in mass number } 238 - 206 = 32$$

$$\text{Number of } \alpha\text{-particles emitted} = \frac{32}{4} = 8\alpha$$

Total decrease in atomic number by emission of 8 α -particles

$$= 8 \times 2 = 16$$

$$\text{Actual difference in atomic numbers} = 92 - 82 = 10$$

$$\therefore \text{No. of } \beta\text{-particles emitted} = 16 - 10 = 6 \beta\text{-particles}$$

206 g of Pb is obtained from 238 g U

$$0.1 \text{ g of Pb is obtained from } \frac{238}{206} \times 0.1 \text{ g} = 0.1155 \text{ g}$$

$$\therefore \text{Mass of Uranium rock} = N_0 = 1 + 0.1155 = 1.1155 \text{ g}$$

$$\begin{aligned} t &= \frac{2.303}{\lambda} \log \frac{N_0}{N_t} \\ &= \frac{2.303}{0.693} \times 4.5 \times 10^9 \text{ years} \log \frac{1.1155}{1} \\ &= 7.0735 \times 10^8 \text{ years.} \end{aligned}$$

Problem 42. Cu (half-life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-life for each of the decay processes. (IIT/JEE 2002)

Solution. The nuclear reactions occurring are :



Let r_1 , r_2 and r_3 are the respective rates of decay of ${}^{64}\text{Cu}$ and r is the over-all rate of decay.

$$\therefore r = r_1 + r_2 + r_3$$

$$k[\text{Cu}] = k_1[\text{Cu}] + k_2[\text{Cu}] + k_3[\text{Cu}]$$

$$\text{or } k = k_1 + k_2 + k_3 \quad \dots(i)$$

where k_1 , k_2 , k_3 and k are the decay-constant for the respective processes.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.8 \text{ h}} = 5.414 \times 10^{-2} \text{ h}^{-1} \quad \dots(ii)$$

$$\text{Given: } \frac{k_1}{k_3} = \frac{38}{43} = 0.884 \text{ and } \frac{k_2}{k_3} = \frac{19}{43} = 0.442$$

Substituting these values in eq (i), one has

$$k = 0.884 k_3 + 0.442 k_3 + k_3 = 2.326 k_3$$

$$(i) k_3 = \frac{k}{2.326} = \frac{5.414 \times 10^{-2} \text{ h}^{-1}}{2.326} = 2.328 \times 10^{-2} \text{ h}^{-1}$$



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Mass-Energy Conversion

- Einstein law for conservation of mass and energy.** This law states that matter can be converted into energy and energy can be converted into matter. Also, the sum of matter and energy transformed is equal to the sum of matter and energy obtained by this transformation.

The conversion of mass into energy and vice-versa is quantitatively related and is given by the following expression :

$$E = mc^2$$

where, E = energy in joules
 m = mass in kilograms
 c = velocity of light
 $= 3.0 \times 10^8 \text{ m sec}^{-1}$.

- Mass-defect.** A stable nucleus has less energy than its constituent particles. The difference in mass of the constituent particles and the stable nucleus is called the mass-defect.

$$\begin{aligned} \text{Mass-defect} &= \Delta m \\ &= \text{Sum of masses of protons and neutrons} - \text{mass of stable nucleus} \end{aligned}$$

- Binding-energy.** It is the energy released when constituent particles join together to form atomic nucleus and is a measure of the stability of the nucleus. Larger the mass-defect, greater the binding-energy and more stable is the nucleus.

$$\text{Binding-energy} = \text{Mass-defect} \times c^2$$

$$\text{Binding-energy per nucleon} = \frac{\text{Total binding-energy}}{\text{Number of nucleons}}$$

- Packing-fraction.** It is a measure of the stability of the atomic nucleus. Greater the negative value of packing fraction, greater is the stability associated with the nucleus. It is given by the following relation :

$$\text{Packing fraction} = \frac{\text{Actual mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

- Conversion factors.**

$$\begin{aligned} 1 \text{ atomic-mass unit} &= 1.6605 \times 10^{-27} \text{ kg} \\ 1 \text{ atomic-mass unit} &= 931.5 \text{ MeV} \\ 1 \text{ eV} &= 1.602 \times 10^{-19} \text{ joules.} \end{aligned}$$

✓ SOLVED PROBLEMS

Problem 1. Find the nuclear binding energy for ${}^9_4\text{Be}$. $m_p = 1.00728 \text{ amu}$, $m_n = 1.00867 \text{ amu}$. The nuclear mass of ${}^9_4\text{Be}$ is 9.00999 amu .



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PROBLEMS FOR PRACTICE

1. Find the nuclear binding energy per nucleon in MeV for ${}^9_4\text{F}$. The nuclear mass of ${}^9_4\text{F}$ is 18.99346, $m_n = 1.00867$ amu, $m_p = 1.00728$ amu.
2. Calculate the total binding energy in J/mol for ${}^{98}_{43}\text{Tc}$. The mass of ${}^{98}_{43}\text{Tc}$ is 98.88264 amu, $m_p = 1.00728$ amu, $m_n = 1.00867$ amu.
3. What is the energy change in J/mol for the following nuclear reaction :



$$m_p = 1.00728 \text{ amu} ; m_n = 1.00867 \text{ amu}.$$

4. The mass of ${}^{64}\text{Zn}$ is 63.91268 amu. Calculate its packing fraction.
5. Calculate the mass loss and the energy released in the α -decay of plutonium-239 (mass = 239.065216 amu). The mass of uranium-235 is 235.04393 amu.
6. Calculate the mass defect and binding energy of ${}^{12}_6\text{C}$. The isotopic weight of carbon is 12.0038 amu. The mass of ${}^1_1\text{H} = 1.0081$ amu and that of neutron is 1.0089 amu. 1 amu = 931 MeV.

ANSWERS

1. 7.78 MeV

2. 8.199×10^3 J/mol3. 1.251×10^{11} J mol $^{-1}$

4. -13.643

5. 0.00673 amu, 6.31 MeV

6. 0.0982 amu, 91.42 MeV.



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12. Wet gases. The gases collected over water in a closed tube contains water vapour as well and therefore Dalton's law of partial pressure says .

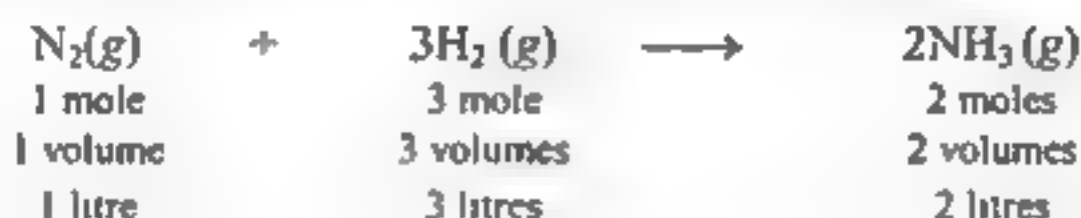
$$P_{\text{Total}} = P_{\text{Moist gas}} = p_{\text{dry gas}} + p_{\text{water vapour}}$$

or

$$p_{\text{dry gas}} = P_{\text{Moist gas}} - p_{\text{water vapour}}$$

$$= P_{\text{Moist gas}} - \text{aqueous tension of water}$$

13. Avogadro's law. A Avogadro, in 1811, proposed that equal volumes of gases at the same temperature and pressure contain equal number of molecules. Conversely, equal numbers of molecules of all the gases at the same temperature and pressure occupy equal volumes.



14. The molar volume or Gram-molecular volume (GMV). 1 mole of a gas contains 6.023×10^{23} molecules and occupy a volume of 22.4 litres at STP. Or 22.4 litres of a gas at STP weigh equal to one gram-mole (Molecular mass expressed in grams).

One mole of O_2 (32 g) occupies 22.4 litres at STP.

One mole of NH_3 (17 g) occupies 22.4 litres at STP.

15. Gay Lussac's law of combining volumes (1808). This law states that when gases combine together at constant temperature and pressure, they do so in volumes which bear a simple ratio to each other and to the volume of the gaseous products.



✓ SOLVED PROBLEMS

Problem 1. A given amount of a gas occupies a volume of 200 ml at a pressure of 700 mm Hg at 25°C . What would be the volume of the gas if the pressure increases to 1000 mm Hg at 25°C ?

Solution.

$$P_1 = \text{Initial pressure} = 700 \text{ mm}$$

$$V_1 = \text{Initial volume} = 200 \text{ mL}$$

$$P_2 = \text{Final pressure} = 1000 \text{ mm}$$

$$V_2 = \text{Final volume} = ?$$

Since temperature is constant, Boyle's law is applied

$$P_1 V_1 = P_2 V_2$$

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{700 \text{ mm} \times 200 \text{ mL}}{1000 \text{ mm}} = 140 \text{ mL.}$$

Problem 2. The gas in outer space is at a pressure of 5×10^{-14} torr. When the temperature is constant, how much outer space could you compress into 1 dm^3 box at 1 atmosphere ?

Solution.

$$P_1 = 5 \times 10^{-14} \text{ torr}; \quad V_1 = ?$$

$$P_2 = 1 \text{ atm} = 760 \text{ torr}; \quad V_2 = 1 \text{ dm}^3$$

$$P_1 V_1 = P_2 V_2$$

at constant temperature



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$$\frac{n_1}{n_2} = \frac{T_2}{T_1} \quad \text{or} \quad T_2 = \frac{n_1}{n_2} \times T_1$$

$$= \frac{1 \text{ mol}}{0.4 \text{ mol}} \times 300 \text{ K} = 750 \text{ K}$$

$$\therefore \text{Temperature in } ^\circ\text{C} = 750 - 273 = 477^\circ\text{C}.$$

Problem 13. 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas?

(IIT/JEE 1979)

Solution. $PV = nRT = \frac{m}{M} RT$

$$T = 273 + 1^\circ\text{C}.$$

(a) For hydrogen gas, molecular-mass = 2 g mol^{-1}

$$PV = \frac{0.184 \text{ g}}{2 \text{ g mol}^{-1}} \times R \times 290 \text{ K}$$

(b) For the unknown gas, molecular mass = M

$$PV = \frac{3.7 \text{ g}}{M \text{ g mol}^{-1}} \times R \times 298 \text{ K}$$

As P and V are the same in both the cases,

$$\frac{3.7 \text{ g}}{M \text{ g mol}^{-1}} \times R \times 298 \text{ K} = \frac{0.184 \text{ g}}{2 \text{ g mol}^{-1}} \times R \times 290 \text{ K}$$

or
$$M = \frac{3.7 \times 298 \times 2}{0.184 \times 290} = 41.33 \text{ g/mol}.$$

Problem 14. When 2 g of a gas A is introduced into an evacuated flask kept at 25°C , the pressure is found to be 1 atmosphere. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights $M_A : M_B$.

(IIT/JEE 1983)

Solution. $PV = nRT = \frac{m}{M} RT$

or
$$M = \frac{mRT}{PV}$$

For gas A
$$M_A = 2 \text{ g} \times \frac{RT}{1 \text{ atm} \times V}$$

$$P_{\text{Total}} = P_A + P_B \quad \text{(Volume is constant)}$$

$$1.5 \text{ atm} = 1 \text{ atm} + P_B$$

or
$$P_B = 1.5 - 1.0 = 0.5 \text{ atm}$$

$$\therefore M_B = 3 \text{ g} \times \frac{RT}{0.5 \text{ atm} \times V}$$

$$\frac{M_A}{M_B} = \frac{2 \text{ g} \times RT}{1 \text{ atm} \times V} \times \frac{0.5 \text{ atm} \times V}{3 \text{ g} \times RT} = \frac{1}{3}$$

$$M_A : M_B :: 1 : 3$$



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Problem 22. A rigid container holds H_2 at 700 mm Hg and $\text{SO}_2(\text{g})$ at 200 mm of Hg and 1500°C . The gases react according to the equation :



What is the pressure in the container at 1500°C when the reaction is complete?

Solution. $PV = nRT$

At constant volume and temperature

$$P \propto \text{number of moles}$$

The reaction is :



The equation tells that 3 moles of H_2 combine with 1 mole of SO_2 to form 1 mole of H_2S and 2 moles of $\text{H}_2\text{O}(\text{g})$. Let 200 A moles of SO_2 combine with $(200 \times 3) A = 600 A$ moles of H_2 to form 200 A moles of H_2S and $(200 \times 2) A = 400 A$ moles of $\text{H}_2\text{O}(\text{g})$.

As pressure \propto number of moles

$$\therefore P_{\text{SO}_2} \text{ after reaction} = 200 \text{ mm} - 200 \text{ mm} = 0$$

$$P_{\text{H}_2} \text{ after reaction} = 700 \text{ mm} - (200 \text{ mm} \times 3) = 100 \text{ mm}$$

$$P_{\text{H}_2\text{S}} = 200 \text{ mm}$$

$$P_{\text{H}_2\text{O}} = 200 \text{ mm} \times 2 = 400 \text{ mm}$$

$$P_{\text{Total}} = P_{\text{SO}_2} + P_{\text{H}_2} + P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}}$$

$$= 0 + 100 \text{ mm} + 200 \text{ mm} + 400 \text{ mm} = 700 \text{ mm.}$$

Problem 23. A rigid container holds a mixture of 5% H_2 , 20% N_2 and 75% NH_3 at 750 mm of Hg and 300°C . What is the partial pressure of each gas in the mixture ?

$$\text{Solution. Partial pressure} = \frac{\text{Total pressure} \times \text{percentage}}{100}$$

$$P_{\text{H}_2} = \frac{750 \text{ mm} \times 5}{100} = 37.5 \text{ mm}$$

$$P_{\text{N}_2} = \frac{750 \text{ mm} \times 20}{100} = 150 \text{ mm}$$

$$P_{\text{NH}_3} = \frac{750 \text{ mm} \times 75}{100} = 562.5 \text{ mm.}$$

Problem 24. 3.2 g methanol when introduced into a hot chamber of volume 0.3 litre at high temperature (600 K) decomposes partially according to the following equation:



At 600 K, the pressure in the hot chamber is 32 atm. What is the percent dissociation of methanol ?

Solution. $PV = nRT$

$$\text{Number of moles of all the gases in the chamber} = \frac{PV}{RT}$$

$$= \frac{32 \text{ atm} \times 0.3 \text{ litre}}{0.082 \text{ atm L K}^{-1} \text{ mol}^{-1} \times 600 \text{ K}} = 0.195 \text{ mol.}$$



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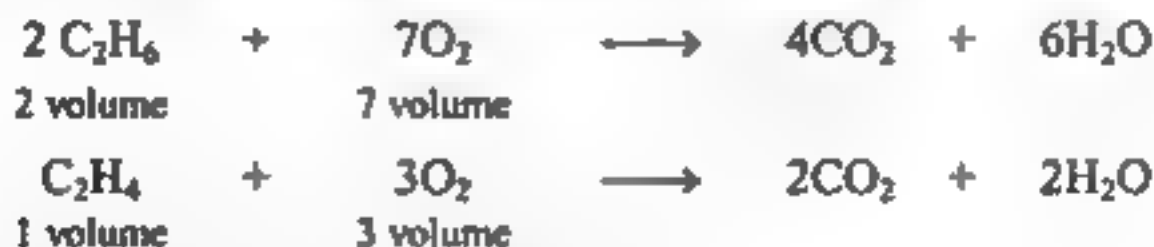


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Problem 31. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litres at 1.00 atm at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O . Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture. (IIT/JEE 1995)

Solution. Let the volume of ethane in the mixture = V litres

\therefore Volume of ethene in the mixture = $(40 - V)$ litres



2 volume C_2H_6 reacts with 7 volume O_2

V litres C_2H_6 reacts with $\frac{7}{2} V$ litres O_2

1 volume C_2H_4 reacts with 3 volume O_2

$(40 - V)$ litres C_2H_4 reacts with $3(40 - V)$ litres O_2

$$32 \text{ g } O_2 = 1 \text{ mol } O_2$$

$$130 \text{ g } O_2 = \frac{1 \text{ mol} \times 130 \text{ g}}{32 \text{ g}}$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$= \frac{130 \text{ mol}}{32} \times \frac{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}{1 \text{ atm}} = 133.25 \text{ L}$$

$$\therefore \frac{7}{2} V + 3(40 - V) = 133.25 \text{ L}$$

$$\frac{7}{2} V + 120 - 3V = 133.25 \text{ L}$$

$$0.5 V = 13.25 \text{ L}$$

$$V = \frac{13.25}{0.5} = 26.5 \text{ L}$$

$$40 - V = 40 \text{ L} - 26.5 \text{ L} = 13.5 \text{ L}$$

$$\therefore \text{Mole fraction } C_2H_6 = \frac{26.5 \text{ L}}{40 \text{ L}} = 0.6625$$

$$\text{Mole fraction } C_2H_4 = \frac{13.5 \text{ L}}{40 \text{ L}} = 0.3375$$

Problem 32. An iron cylinder contains helium at a pressure of 250 k Pa at 300 K. The cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. (M.P. of the cylinder = 1800 K) (Roorkee 1995)

Solution. $P_1 = 250 \text{ k Pa}; P_2 = ?$



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PROBLEMS FOR PRACTICE

1. A gas is expanded at constant temperature from an initial volume of 300 mL to a final volume of 1 litre where its pressure is 0.15 atm. What was the original pressure ?
2. 12.0 litres of helium gas at 1.5 atmosphere is squeezed into a meteorological balloon of 1.2 litres. How much pressure needs to be applied if the temperature does not change?
3. A balloon containing 3 litres of hydrogen gas at 750 mm Hg pressure. After 4 hours, the pressure of the gas was found to be 720 mm Hg. How much is the expansion in the volume of the balloon ? Assume temperature constant.
4. A given quantity of a gas at 760 mm Hg pressure and a temperature of 25°C occupies a volume of 3.5 litres. What is the volume of the same amount of the gas at 35°C and 760 mm Hg pressure ?
5. A gas with a volume of 200 litres is under a pressure of 2 atmosphere at 20°C . What temperature would be required to triple the pressure without changing the volume ?
6. A gas with a volume of 2 litres is cooled at a constant pressure from 1000°C to 0°C . What volume will it occupy now ?
7. What is the volume at STP of a gas that occupies 100 mL at 23°C and 800 mm Hg pressure ?
8. A sealed iron container containing 0.4 dm^3 of nitrogen gas at 25°C and 0.99 atm pressure is thrown into a fire where the temperature is 1100°C . What will be the new pressure of the gas in the container ? Assume constant volume and ideal behaviour.
9. 700 mL of a gas at 20°C and 755 torr is pumped into a vessel of 400 mL at 25°C . What is the pressure of the gas in the vessel ?
10. What is the temperature of a sample of 4.0 moles of a gas occupying a volume of 8.0 litres at 740 mm Hg pressure ?
11. Calculate the pressure of 4.4 g CO_2 in a 5 litre container at 0°C .
12. What is the volume occupied by 3.5 g of oxygen gas at 30°C and 750 torr ?
13. Hydrogen is filled in 224 mL container at 0°C and one atmosphere. Calculate the number of molecules of hydrogen in the container.
14. 10 moles of oxygen are confined in a vessel with a capacity of 224 litres. If the temperature is 0°C , what is the pressure ?
15. Nitrous oxide gas is present in a 5.0 litre rigid container at a pressure of 7.6×10^{-3} torr. Calculate the number of nitrous oxide molecules in the container at -10°C ?
16. An open vessel containing 15 moles of air at 25°C is cooled until the total number of moles becomes 25. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been cooled.
17. 50.0 g of a gas at 30°C occupied the same volume as 25 g of oxygen at 20°C and at the same pressure. What is the molecular mass of the gas ?
18. The volume occupied by the vapour when 12.4 g of white phosphorus is vaporized at 280.3°C at 715 mm Hg pressure is 4.82 litres. What is the molecular formula of phosphorus vapour under these conditions?
19. The mass of 400 mL of a triatomic gas at 20°C and 0.611 atm pressure is 0.48 g. Calculate the mass in g of one atom.
20. The total pressure of a sample of nitrous oxide gas over water is 745 mm Hg at 35°C .



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(e) For the gases that diffuse in the same time, t

$$t_A = t_B = t$$

$$r_A = \frac{V_A}{t} \quad \dots(i)$$

$$r_B = \frac{V_B}{t} \quad \dots(ii)$$

Dividing eq. (i) by eq. (ii), one has

or
$$\frac{r_A}{r_B} = \frac{V_A}{V_B} \times \frac{t}{t} = \frac{V_A}{V_B}$$

Now as
$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$$

$$\boxed{\frac{r_A}{r_B} = \frac{V_A}{V_B} = \sqrt{\frac{d_B}{d_A}}}$$

(f) *Relationship between rate of diffusion of a gas and temperature* The rate of diffusion of a gas is directly proportional to the square root of its temperature in Kelvin.

$$\boxed{\frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{T_1}{T_2}}} \quad \text{(at constant pressure)}$$

8. **Relative (vapour) density of a gas, $A = \frac{\text{Density of A}}{\text{Density of hydrogen}}$**

9. **Relation between density and temperature of a gas**

$$\text{Density, } d = \frac{\text{Mass}}{\text{Volume}} \quad \text{or} \quad d \propto \frac{1}{V} \quad \dots(i)$$

According to Charle's law when pressure is constant

$$V \propto T \quad \dots(ii)$$

Combining eq. (i) and (ii), one has

$$d \propto \frac{1}{T}$$

or $dT = \text{constant}$

or $\boxed{d_1 T_1 = d_2 T_2}$

10. **Relation between density, temperature and pressure of a gas.**

$$d \propto \frac{1}{T} \quad \dots(i)$$

According to Boyle's law

$$p \propto \frac{1}{V} \quad \text{and} \quad d \propto \frac{1}{V}$$

$$d \propto P \quad \dots(ii)$$



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Problem 3. Calculate the density of ammonia gas at 30°C and 5 atm pressure.

(IIT/JEE 1978)

Solution.

$$PV = nRT = \frac{g}{M} RT$$

$$d = \frac{g}{V} = \frac{PM}{RT} = \frac{5.0 \text{ atm} \times 17.0 \text{ g mol}^{-1}}{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 303 \text{ K}}$$

$$= 3.42 \text{ g litre}^{-1}$$

Problem 4. The density of a gas, X, is 2.50 g/litre at 40°C and 740 mm Hg. What is the molecular mass of the gas?

Solution. $T = 273 + 40^\circ\text{C} = 313 \text{ K}$

$$PV = nRT = \frac{g}{M} RT$$

$$d = \frac{PM}{RT}$$

$$M = \frac{dRT}{P} = \frac{2.50 \text{ g litre}^{-1} \times 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 313 \text{ K}}{740/760 \text{ atm}}$$

$$= 65.89 \text{ g mol}^{-1}$$

Problem 5. What is the density of SO_2 at STP?

Solution. Molecular mass of $\text{SO}_2 = 32 + 2 \times 16 = 64 \text{ g mol}^{-1}$

The volume of 1 mole of a gas at STP is 22.4 litres.

$$\text{density of SO}_2 \text{ at STP} = \frac{\text{Mass in g}}{\text{Volume of the gas in litre}} = \frac{64.0 \text{ g}}{22.4 \text{ litres}}$$

$$= 2.86 \text{ g/litre.}$$

Problem 6. The density of a gas, X, is 3.5 g/litre at 10°C and 730 mm Hg. What will be its density at -10°C and 720 mm Hg?

Solution.

$$\frac{d_1 T_1}{P_1} = \frac{d_2 T_2}{P_2}$$

$$d_1 = 3.5 \text{ g/litre}; \quad P_1 = 730 \text{ mm}; \quad T_1 = 273 + 10^\circ\text{C} = 283 \text{ K}$$

$$d_2 = ?; \quad P_2 = 720 \text{ mm}; \quad T_2 = 273 + (-10^\circ\text{C}) = 263 \text{ K}$$

$$d_2 = \frac{d_1 T_1}{P_1} \times \frac{P_2}{T_2} = \frac{3.5 \text{ g/litre} \times 283 \text{ K} \times 720 \text{ mm}}{730 \text{ mm} \times 263 \text{ K}}$$

$$= 3.71 \text{ g/litre.}$$

Problem 7. The density of a gas, X, is 1.5 g/litre at 25°C and 0.9 atm. At what temperature its density will be 2.5 g/litre when pressure is kept constant?

Solution. $d_1 = 1.5 \text{ g/litre}, T_1 = 273 + 25^\circ\text{C} = 298 \text{ K}; d_2 = 2.5 \text{ g/litre}; T_2 = ?$

$$d_1 T_1 = d_2 T_2 \quad \text{at constant pressure}$$

$$T_2 = \frac{d_1 T_1}{d_2} = \frac{1.5 \text{ g/litre} \times 298 \text{ K}}{2.5 \text{ g/litre}} = 178.8 \text{ K}$$

$$t^\circ\text{C} = 178.8 - 273 = -94.2^\circ\text{C.}$$



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Problem 24. A 4:1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially? (IIT/JEE 1994)

Solution.

Rate of diffusion $\propto \mu$ (average kinetic energy of molecules)

$$\propto \sqrt{\frac{P}{M}}$$

$$\therefore \frac{\text{Rate of diffusion of gas A } (\mu_1)}{\text{Rate of diffusion of gas B } (\mu_2)} = \sqrt{\frac{P_A \times M_B}{M_A \times P_B}}$$

$$\frac{\mu_1}{\mu_2} = \sqrt{\frac{P_{\text{He}} \times M_{\text{CH}_4}}{M_{\text{He}} \times P_{\text{CH}_4}}}$$

$$\text{Partial pressure of He } (p_{\text{He}}) = \text{Mole fraction} \times P_{\text{Total}}$$

$$= \left(\frac{4}{4+1} \right) 20 \text{ bar} = 16 \text{ bar}$$

$$\text{Partial pressure of CH}_4 (p_{\text{CH}_4}) = \left(\frac{1}{4+1} \right) 20 \text{ bar} = 4 \text{ bar}$$

$$\frac{\mu_1}{\mu_2} = \sqrt{\frac{16 \text{ bar} \times 16 \text{ g/mol}}{4 \text{ g/mol} \times 4 \text{ bar}}} = \frac{4}{1}$$

The ratio of moles of He and CH_4 in the mixture effusing out initially is 4 : 1.

Problem 25. The composition of the equilibrium mixture ($\text{Cl}_2 \rightleftharpoons 2\text{Cl}$), which is attained at 1200°C , is determined by measuring the rate of effusion through a pin-hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as Krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (Atomic wt. of Kr = 84). (IIT/JEE 1995)

Solution.

$$\frac{r_{\text{Kr}}}{r_{\text{mix}}} = \sqrt{\frac{M_{\text{ave (mixture)}}}{M_{\text{Kr}}}}$$

$$M_{\text{ave}} = \left(\frac{r_{\text{Kr}}}{r_{\text{mix}}} \right)^2 \times M_{\text{Kr}}$$

$$= \left(\frac{1}{1.16} \right)^2 \times 84 \text{ g/mol} = 62.42 \text{ g/mol}$$



$$M_{\text{ave}} = x_{\text{Cl}} M_{\text{Cl}} + x_{\text{Cl}_2} M_{\text{Cl}_2}$$

$$= \frac{2x}{1+x} M_{\text{Cl}} + \frac{(1-x)}{1+x} M_{\text{Cl}_2}$$

$$M_{\text{ave}} = \frac{2x M_{\text{Cl}} + (1-x) M_{\text{Cl}_2}}{1+x}$$



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- same temperature and pressure. If the density of hydrogen is 0.09 g/litre, what is the density of the gas ?
20. The ratio of the rates of diffusion of hydrogen and a gas, X , are 7:2. What is the density of the gas at STP ? What is its molecular mass ?
 21. Calculate the relative rates of diffusion of NO and NO_2 gases.
 22. 2 litres of a gas diffuse in the same time as 3 litres of chlorine at 60°C and 745 mm Hg pressure.
 - (a) What is the molecular mass of the gas ?
 - (b) What is the density of the gas at 60°C and 745 mm Hg pressure ?
 23. 80 volumes of ammonia gas effuse out from a vessel in 8 minutes at -5°C and 500 mm Hg pressure. How long will 40 volumes of a certain gas, X , with molecular mass 68 take to effuse out from the same vessel at the same temperature and pressure ?
 24. 950 mL of propane gas diffuse through a porous plug in 1200 seconds. What volume of nitrogen would diffuse in the same time ?
 25. 450 mL of a gas, X , was mixed with 75 mL of helium and the mixture allowed to diffuse through a porous plug in an atmosphere of helium. 45 mL of the gas, X , was found to diffuse in 4.5 minutes. Under the same conditions 90 mL of oxygen diffused out of 270 mL in the same time. What is the molecular-mass of gas, X ?
 26. 5 Litres of a gas, A , diffuse through a porous plug in 40 minutes. Under the same conditions, 5 litres of a mixture of two gases A and 40% by volume of B diffuses in 50 minutes. If the density of A is 3.0 g/litre, what is the density of gas, B ?
 27. Two cotton wads, one soaked with NH_3 solution and the other soaked with hydrochloric acid are inserted in opposite ends of a one metre long glass tube. A white cloud of NH_4Cl appears after some time at a distance of 0.6 metre from the end containing wad soaked with ammonia. Calculate the relative rates of diffusion of NH_3 and HCl gases.
 28. NH_3 gas and HCl gas at the same pressure at 31°C are allowed to effuse through identical pin holes from opposite ends of a glass tube of 3 metre length. A cloud of ammonium chloride first forms at a point P inside the tube. Find the distance of the point P from the end through which HCl effused.
 29. A straight glass tube has two identical inlets X and Y at the two ends. The length of the tube is 2.0 metre. NH_3 gas at P atm and HCl gas at 2 atm pressure are allowed to effuse through the pin holes from the opposite ends at the same time. NH_4Cl is first formed at a distance of 1.29 m from the end through which NH_3 gas is sent in. What is the value of P ?
 30. The pressure in a bulb dropped from 1200 to 700 torr to 50 minutes when the contained A gas leaked through a small hole. The same bulb was evacuated and then filled with gas, X , at a pressure of 1500 torr. After 50 minutes, the drop in pressure was found to be 300 torr. Find the ratio of the rates of diffusion of A and X .
 31. The pressure in a bulb dropped from 3000 torr to 2000 torr in 50 minutes when the contained chlorine leaked through a small hole. The bulb was then evacuated and another gas with molecular mass of 213 in the molar ratio of 1 : 1 at a total pressure of 6000 torr was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 25 minutes.



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$$3. (a) \text{ Root mean square velocity } (\mu) = \sqrt{\frac{3RT}{M}}$$

$$\text{Average velocity } (V) = \sqrt{\frac{8RT}{\pi M}}$$

$$\text{Most probable velocity } (\alpha) = \sqrt{\frac{2RT}{M}}$$

$$\mu : V : \alpha = 1.00 : 0.92 : 0.82$$

$$(a) \quad \text{Average-velocity} = 0.92 \times \text{Root mean square velocity}$$

$$(b) \quad \text{Most probable velocity} = 0.82 \times \text{Root mean square velocity}$$

$$4. (a) \text{ Kinetic-energy of a molecule} = \frac{1}{2} m \mu^2$$

where, m = Mass of the molecule

μ = Root mean square velocity

$$(b) \quad \text{Kinetic-energy (K.E.)} = \frac{3}{2} RT \quad (\text{For 1 mole})$$

$$\text{K.E.} = \frac{3}{2} n RT \quad (\text{for } n \text{ moles})$$

where, n = Number of moles of the gas

T = Absolute temperature

R = Gas constant

$$(c) \quad \text{K.E.} = \frac{3}{2} \frac{R}{N} T \quad (\text{for 1 molecule})$$

where N is Avogadro number

$$\text{K.E.} = \frac{3}{2} kT$$

where k is Boltzmann-constant $= 1.381 \times 10^{-16}$ erg per molecule K

$$5. \quad PV = \frac{1}{3} nm \mu^2 = \left(\frac{2}{3} n \right) \left(\frac{1}{2} m \mu^2 \right) = \left(\frac{2}{3} n \right) (\text{K.E.})$$

$$6. \quad \text{K.E.} = \frac{3}{2} RT. \text{ This equation indicates that}$$

(a) All the gases have the same average kinetic-energy (Total K.E.) at the same temperature.

$$(b) \text{ Average kinetic energy for } n \text{ molecules} \quad \frac{1}{2} nm \mu^2 \propto \mu^2$$

$$\mu^2 \propto T$$

$$\text{or} \quad \mu \propto \sqrt{T}$$

7.

$$\mu (\text{rms}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$



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$$\begin{aligned}
 PV &= RT = \frac{1}{3} n m \mu^2 \quad (\text{for 'n' mole}) \\
 n &= \frac{3 RT}{m \mu^2} = \frac{3}{2} \times \frac{2 RT}{m \mu^2} = \frac{3}{2} \frac{RT}{KE} \\
 &= \frac{3 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 263 \text{ K}}{2 \times 544.6 \times 10^{-23} \text{ J}} = 6.023 \times 10^{23} \text{ molecules.}
 \end{aligned}$$

Problem 5. What is the translational energy (kinetic energy) of 150 molecules of N_2O at 30°C ?

Solution.

$$T = 273 + 30^\circ\text{C} = 303 \text{ K}$$

$$\text{K.E.} = \frac{3}{2} RT \quad (\text{for 1 mole of gas})$$

$$\text{K.E.} = \frac{3}{2} \frac{R}{N} T \quad (\text{for 1 molecule})$$

$$= \frac{3}{2} \frac{RT}{N} \times \text{Number of molecules}$$

$$= \frac{3}{2} \times \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 303 \text{ K} \times 150 \text{ molecules}}{(6.023 \times 10^{23} \text{ molecules})}$$

$$= 9.257 \times 10^{-19} \text{ J.}$$

Problem 6. Calculate the total kinetic energy of translation of molecules of chlorine gas per cc at STP. Density of Hg = 13.6 g/cc; $g = 980 \text{ cm sec}^{-2}$.

Solution.

$$T = 273 + 0^\circ\text{C} = 273 \text{ K}$$

1 mole of a gas occupies 22.4 litres at STP,

K.E. of 22400 cc of a gas at STP = K.E. of 1 mole of the gas at 0°C

$$= \frac{3}{2} RT = \frac{3}{2} \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 273 \text{ K}$$

$$= 3404.6 \text{ joules.}$$

$$\text{K.E. of 1 cc of a gas,} = \frac{\text{K.E.}}{22400 \text{ cc}} = \frac{3404.6 \text{ J}}{22400 \text{ cc}} = 0.152 \text{ J/cc.}$$

Problem 7. In a sample of a gas at -8°C and 650 torr in a rigid vessel of 1 litre, 10 molecules move with a velocity of 8 m sec^{-1} , 20 molecules with a velocity of 4 m sec^{-1} and 5 molecules with a velocity of 5 m sec^{-1} . Calculate the root mean square velocity, average velocity and most probable velocity.

Solution.

$$u_{\text{rms}} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + \dots + V_n^2}{n}}$$

$$= \sqrt{\frac{10(8)^2 + 20(4)^2 + 5(5)^2}{10 + 20 + 5}}$$

$$= \sqrt{\frac{640 + 320 + 125}{35}}$$



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Problem 16. The molecules of gas A are moving at twice the speed of molecules of gas B at the same temperature. What is the relationship between molecules of A and B?

Solution.

$$\frac{V_A}{V_B} = \sqrt{\frac{m_B}{m_A}}$$

$$\left(\frac{V_A}{V_B}\right)^2 = \frac{m_B}{m_A} = \left(\frac{2}{1}\right)^2 = 4 \quad \text{or} \quad m_A = \frac{1}{4} m_B$$

Problem 17. Consider samples of H_2 and O_2 gases in separate containers. H_2 is in a 1 litre container at STP. O_2 gas is in a 1 litre container at $0^\circ C$ and 2 atmosphere pressure. Compare quantitatively the total number of collisions per second with the walls.

Solution. (a) $PV = nRT$

When V , R and T are identical,

$$\frac{P_{O_2}}{P_{H_2}} = \frac{n_{O_2}}{n_{H_2}} = \frac{2 \text{ atm}}{1 \text{ atm}} = 2$$

$$n_{O_2} = 2n_{H_2}$$

(b) $\frac{V_{H_2}}{V_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$

or $V_{H_2} = 4V_{O_2}$

(c) Number of collisions \propto Average velocity \times number of molecules

$$C_A \propto V_A n_A$$

$$C_{H_2} \propto V_{H_2} n_{H_2}$$

$$C_{O_2} \propto V_{O_2} n_{O_2}$$

$$\frac{C_{H_2}}{C_{O_2}} = \frac{V_{H_2} n_{H_2}}{V_{O_2} n_{O_2}} = \frac{4V_{O_2} n_{H_2}}{V_{O_2} 2n_{H_2}} = 2.$$

Number of collisions for $H_2 = 2 \times$ Number of collisions for O_2

Problem 18. A 5-litre flask contains 5 moles of carbon dioxide at $27^\circ C$. What is the pressure exerted by the gas? a and b for carbon dioxide are $3.60 \text{ atm. litre}^2 \text{ mol}^{-2}$ and $0.0427 \text{ litre mol}^{-1}$.

Solution. $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

$$P = \frac{nRT}{V - nb} - \frac{a n^2}{V^2}$$

$$= \frac{5 \times 0.082 \times 300}{5 - (5 \times 0.0427)} - \frac{3.60 \times (5)^2}{(5)^2}$$

$$= 25.70 - 3.60 = 22.1 \text{ atm.}$$

Problem 19. What is the volume of 1 mole of hydrogen at 5 atm and $0^\circ C$ if a is $0.245 \text{ atm litre}^2 \text{ mol}^{-2}$ and b is $0.0266 \text{ litre mol}^{-1}$?



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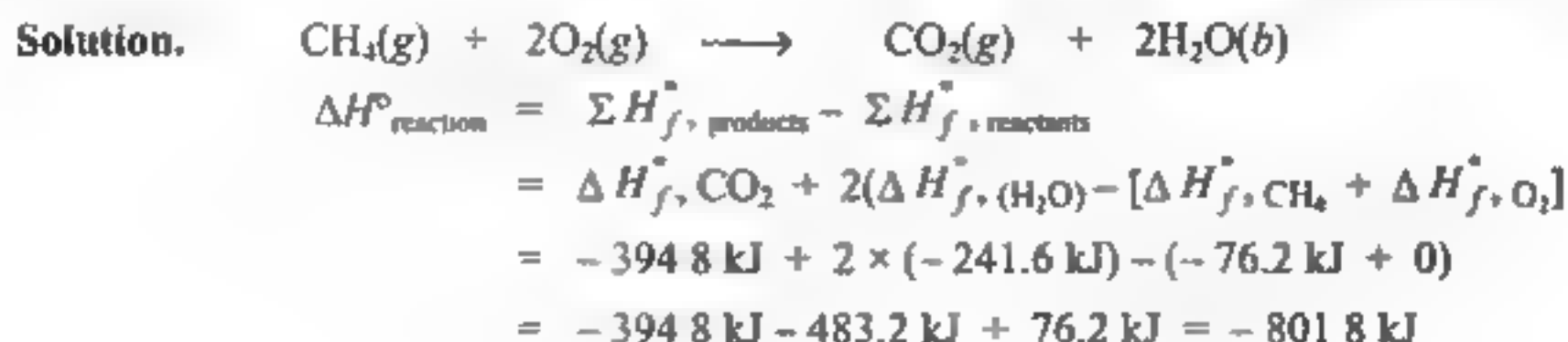
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$$1 \text{ m} = 100 \text{ cm}$$

$$1 \text{ m}^3 = (100 \text{ cm})^3 = 10^6 \text{ cm}^3$$

$$1 \text{ mol} = 22400 \text{ cm}^3 \text{ at STP}$$

$$10^6 \text{ cm}^3 = \frac{1 \text{ mol} \times 10^6 \text{ cm}^3}{22400 \text{ cm}^3} = 44.64 \text{ mol CH}_4$$

Burning of 1 mol CH_4 evolves 801.8 kJ heat

$$\text{Burning of } 44.64 \text{ mol CH}_4 \text{ evolves } \frac{801.8 \text{ kJ}}{1 \text{ mol}} \times 44.64 \text{ mol} = 3.58 \times 10^4 \text{ kJ.}$$

Problem 12. An athlete is given 100 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) of energy equivalent to 1560 kJ. He utilizes 50 per cent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mol. (IIT/JEE 1989)

Solution. Energy from 100 g glucose = 1560 kJ

$$\text{Energy utilized} = \frac{50\%}{100\%} \times 1560 \text{ kJ} = 780 \text{ kJ}$$

$$\text{Energy not used} = 1560 \text{ kJ} - 780 \text{ kJ} = 780 \text{ kJ}$$

$$\text{Enthalpy of evaporation of water} = 44 \text{ kJ/mol}$$

44 kJ energy evaporates 1 mole water

$$\begin{aligned}\therefore 780 \text{ kJ energy evaporates } \frac{1 \text{ mol} \times 780 \text{ kJ}}{44 \text{ kJ}} &= 17.73 \text{ mol water} \\ &= 17.73 \text{ mol} \times 18 \text{ g/mol} = 319.14 \text{ g water}\end{aligned}$$

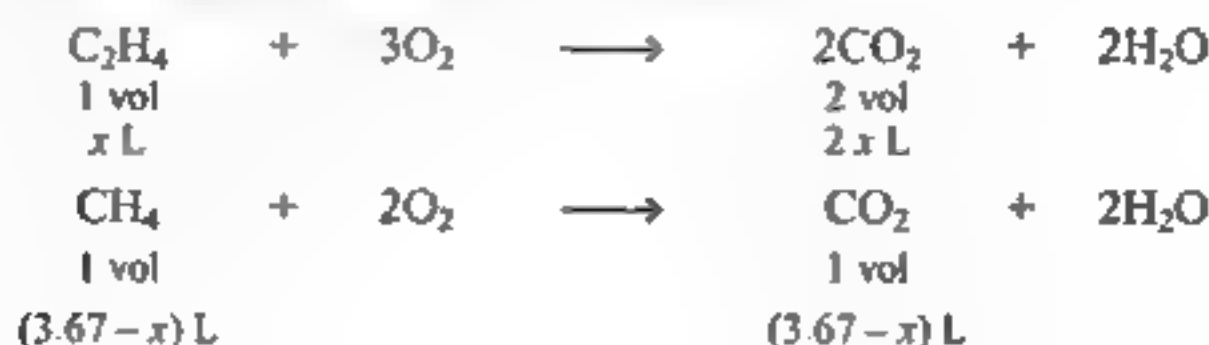
\therefore 319.14 g water is required for perspiration.

Problem 13. A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2 . Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are -1423 and -891 kJ mol^{-1} at 25°C . (IIT/JEE 1991)

Solution. Total volume of the mixture of ethylene and methane = 3.67 L

Let volume of ethylene in the mixture = x L

\therefore Volume of methane in the mixture = $(3.67 - x)$ L





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Chemical Thermodynamics

1. Thermodynamics. It is the study of relationship between heat and other forms of energy in physical systems or chemical reactions. It tells us whether a physical change or a chemical reaction will occur or not under certain conditions or a substance is stable or unstable under a given set of conditions. It also tells us that the chemical energy of a substance does not depend on the method of preparation or its past history but depends only on its state, i.e., chemical composition, physical state, temperature and pressure etc. These quantities are called *state functions* and can be studied either in an open or closed system. Thermodynamics does not tell us about the time a change or reaction takes to occur or reach a certain stage but tells us:

- (a) Can a physical or chemical change be expected to occur under a given set of conditions?
- (b) How far the change can go?
- (c) If a physical or chemical change occurs, what are the energy changes in the system and the surroundings?

2. System. A system is a specified space which is under thermodynamic studies and is separated from the rest of the universe by a boundary, imaginary or real. The part of the universe outside the system is called its *surroundings*.

3. Types of thermodynamic systems

- (a) **Open system.** A system that exchanges matter and energy with its surroundings is called an open system. Examples are car engines.
- (b) **Closed system.** A system that does not exchange matter with its surroundings is called a closed system. It can transfer energy in the form of heat, work and radiations to the surroundings. Example are chemical reactions carried out in sealed containers.
- (c) **Isolated system.** A system that does not exchange matter or heat with its surroundings is called an isolated system.

4. Types of thermodynamic processes

- (a) **Adiabatic process.** No heat flows in or out of the closed system, i.e., the system does not exchange heat with its surroundings.

$$\text{For an adiabatic process } dq = 0$$

- (b) **Isothermal process.** Heat can flow in or out of the closed system and temperature of the system remains constant. An isothermal process can be carried out by placing the system in a thermostat.

$$\text{For an isothermal process } dT = 0$$

- (c) **Isobaric process.** It takes place at constant pressure. Conversion of liquid water



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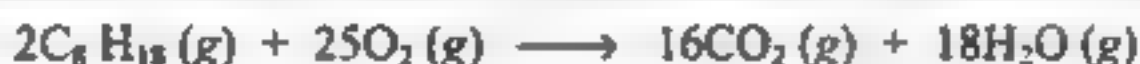
$$E_B - E_A = \Delta E = q + W$$

$$q = \Delta E - W$$

where E_B and E_A are the energies of the system in the final and initial states respectively. ΔE is the change in its internal energy, q is the heat absorbed by the system and W is the work done by the system by spending some of the energy absorbed.

$$\begin{aligned} q &= \Delta E + W_{\text{expansion}} + W_{\text{non-expansion}} \\ &= \Delta E + W_{\text{expansion}} + W_{\text{useful work}} \end{aligned}$$

17. Expansion and contraction work. Consider a car cylinder which exchanges both heat and mechanical work with its surroundings. It has a mixture of gasoline and oxygen and is fitted with a spark-plug and a movable piston. The spark-plug on ignition initiates a chemical reaction in which number of moles of the gases increases.



As the gases in the cylinder expand against the piston at a constant external pressure P , they exert a force F and move the piston a certain distance (d).

$$\therefore \text{Work done by the gas system} = W = \text{Force} \times \text{Distance} = F \times d$$

Let A be the surface area of the piston and P the pressure exerted by the gases, As pressure is force per unit area,

$$\text{Pressure } (P) = \frac{\text{Force}}{\text{Area}} = \frac{F}{A}$$

$$F = P \times A$$

$$\text{One has} \quad W = F \times d = P \times A \times d = P \times \Delta V \quad (\because \Delta V = A \times d)$$

$$\text{By convention} \quad W_{\text{exp}} = -P \times \Delta V$$

$$\begin{aligned} \text{Work done on the gas system (Contraction) by the surroundings} \\ = P \times (\Delta V) \end{aligned}$$

Thermodynamic sign conventions.

$$\Delta E = q + W$$

1. When heat is absorbed by the system, q is positive.
2. When heat is given out by the system, q is negative.
3. When work is done by the system (expansion), W is negative.
4. When work is done on the system (contraction) W is positive.

18. Work done in an isothermal change.

$$W = P(V_2 - V_1)$$

where, P is the external pressure

V_1 = Initial volume

V_2 = Final volume

$$\boxed{1 \text{ L-atm} = 101.3 \text{ J}}$$

$$P = h d g$$

$$1 \text{ atm} = 0.76 \text{ m} \times 13.6 \text{ g/cm}^3 \times 9.8 \text{ m sec}^{-2}$$

$$= 101.3 \frac{\text{g}}{\text{cm}^2} \text{ m}^2 \text{ sec}^{-2} = 101.3 \left(\frac{1000 \text{ g}}{1000 \text{ cm}^3} \right) \text{ m}^2 \text{ sec}^{-2}$$

$$= \frac{101.3 \text{ kg m}^2 \text{ sec}^{-2}}{\text{litre}}$$

$$1 \text{ Litre-atm} = 101.3 \text{ J}$$



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$$\begin{aligned}
 PV &= nRT \\
 V &= \frac{nRT}{P} \\
 &= \frac{(1.0 \text{ mol}) (0.082 \text{ L-atm mol}^{-1}) \text{K}^{-1} (373 \text{ K})}{1.0 \text{ atm}} = 31 \text{ Litres} \\
 \Delta V &= \text{Final volume} - \text{Initial volume} = 31 \text{ Litres} \\
 W &= -P_{\text{ext}} \Delta V = -(1.0 \text{ atm}) (31 \text{ L}) (101.3 \text{ J/L-atm}) \\
 &= -3140.3 \text{ J}
 \end{aligned}$$

Problem 7. Calculate the work done by 1.0 mol of an ideal gas when it expands from 10 atmosphere to 2 atmosphere at 27°C.

Solution. $W = -P_{\text{ext}} (V_2 - V_1)$

Using ideal gas equation,

$$\begin{aligned}
 V_2 &= \frac{nRT}{P_2} \text{ and } V_1 = \frac{nRT}{P_1} \\
 \therefore W &= -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right) \\
 &= -P_{\text{ext}} \times nRT \left(\frac{1}{P_2} - \frac{1}{P_1} \right)
 \end{aligned}$$

$$\frac{1}{P_2} - \frac{1}{P_1} = \frac{1}{2} - \frac{1}{10} = \frac{2}{5}$$

$$\begin{aligned}
 W &= -(2.0 \text{ atm}) (1.0 \text{ mol}) (0.082 \text{ L-atm mol}^{-1} \text{K}^{-1}) (300 \text{ K}) \left[\frac{2}{5} \right] \\
 &= -19.68 \text{ L-atm} \\
 &= -19.68 \text{ L-atm} \times 101.3 \text{ J/L-atm} = -1993.6 \text{ J}
 \end{aligned}$$

Problem 8. A 5.0 litre cylinder contained 10 moles of oxygen gas at 40°C. Due to sudden leakage through a hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmospheric pressure is 1.0 atmosphere, calculate the work done by the gas.

Solution. $V_1 = 5.0 \text{ litres}, P_{\text{ext}} = 1.0 \text{ atm}$

$$T = 40^\circ\text{C} + 273 = 313 \text{ K}$$

$$\begin{aligned}
 V_2 &= \frac{nRT}{P} = \frac{(10 \text{ mol}) (0.082 \text{ L-atm mol}^{-1} \text{K}^{-1}) (313 \text{ K})}{1.0 \text{ atm}} \\
 &= 256.66 \text{ litres} \\
 W &= -P_{\text{ext}} (V_2 - V_1) \\
 &= -1.0 \text{ atm} \times (256.66 - 5) \text{ Litres} = -251.66 \text{ L-atm} \\
 &= -251.66 \text{ L-atm} \times 101.3 \text{ J/L-atm} = -25493.2 \text{ J}
 \end{aligned}$$

Problem 9. 2 moles of an ideal gas at 25°C is allowed to expand reversibly at constant temperature (isothermally) from a volume of 2 litres to 10 litres by reducing the pressure slowly. Calculate the work done by the gas (W), ΔE , q and ΔH .



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Solution. $P_1 = 1 \text{ atm}$, $P_2 = 10 \text{ atm}$, $V_1 = 25 \text{ L}$, $V_2 = 10 \text{ L}$

$$\begin{aligned}
 W &= - \frac{P_2 V_2 - P_1 V_1}{1 - \gamma} \\
 &= - \frac{10 \text{ atm} \times 10 \text{ L} - 1 \text{ atm} \times 25 \text{ L}}{1 - 1.4} = - \frac{100 - 25}{-0.4} \text{ L-atm} \\
 &= + \frac{75}{0.4} = 187.5 \text{ L-atm} = 187.5 \text{ L-atm} \times 101.3 \text{ J/L-atm} \\
 &= 18993.8 \text{ J} = 18.9938 \text{ kJ}.
 \end{aligned}$$

Problem 28. 20 g of neon gas occupying a volume of 15 litres at 3.5 atmosphere pressure expands adiabatically to 30 litres. Calculate the work done by the gas. γ is 1.67.

Solution.

$$\begin{aligned}
 \frac{P_2}{P_1} &= \left(\frac{V_1}{V_2} \right)^\gamma \\
 P_2 &= P_1 \times \left(\frac{V_1}{V_2} \right)^\gamma = 3.5 \text{ atm} \times \left(\frac{15 \text{ L}}{30 \text{ L}} \right)^{1.67} \\
 &= 3.5 \times 0.3143 = 1.1 \text{ atm} \\
 W &= - \frac{P_2 V_2 - P_1 V_1}{1 - \gamma} = - \frac{1.1 \text{ atm} \times 30 \text{ L} - 3.5 \text{ atm} \times 15 \text{ L}}{1 - 1.67} \\
 &= - \frac{33 - 52.5}{-0.67} = - 29.1 \text{ L-atm} \\
 &= -29.1 \text{ L-atm} \times 101.3 \text{ J/L-atm} = -2947.8 \text{ J}.
 \end{aligned}$$

Problem 29. Calculate W for the adiabatic reversible expansion of 3 moles of a triatomic gas ($\gamma = 1.33$) at -50°C and 20 atmosphere to a final pressure of 2 atm.

$$R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$$

Solution. (a)

$$\begin{aligned}
 \left(\frac{T_2}{T_1} \right)^\gamma &= \left(\frac{P_2}{P_1} \right)^{\gamma-1} \\
 \left(\frac{T_2}{T_1} \right) &= \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \\
 \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} &= \left(\frac{2 \text{ atm}}{20 \text{ atm}} \right)^{\frac{1.33-1}{1.33}} = \left(\frac{2}{20} \right)^{\frac{0.33}{1.33}} = 0.5649 \\
 T_1 &= -50^\circ\text{C} + 273 = 223 \text{ K} \\
 \frac{T_2}{T_1} &= 0.5649 \\
 T_2 &= 0.5649 \times T_1 = 0.5649 \times 223 \text{ K} = 126 \text{ K} \\
 T_2 - T_1 &= 126 \text{ K} - 223 \text{ K} = -97 \text{ K} \\
 W &= \frac{R}{1 - \gamma} [T_2 - T_1]
 \end{aligned}$$



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$$0 = q - 5227.2 \text{ J}$$

$$\text{or } q = +5227.2 \text{ J}$$

$$\Delta H = \Delta E + \Delta n_g RT, \quad \text{Since } R \text{ and } T \text{ are constants, } \Delta H = 0 + 0 = 0$$

Problem 39. Two moles of a perfect gas undergo the following processes :

- (a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
- (b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
- (c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

(i) Sketch with labels each of the processes on the same p - V diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.

(iii) What will be the values of ΔU , ΔH and ΔS for the overall process ?

(IIT/JEE 2000)

Solution. (i) The p - V diagram of the given processes a , b and c are shown in the fig. below.

(a) Reversible isobaric expansion

$$(1 \text{ atm}, 20 \text{ L}) \longrightarrow (1 \text{ atm}, 40 \text{ L})$$

(b) Reversible isochoric expansion

$$(1 \text{ atm}, 40 \text{ L}) \longrightarrow (0.5 \text{ atm}, 40 \text{ L})$$

(c) Reversible isothermal compression

$$(0.5 \text{ atm}, 40 \text{ L}) \longrightarrow (1 \text{ atm}, 20 \text{ L})$$

(ii) Work involved in the given processes are as follows.

$$\begin{aligned} \text{Process (a)} \quad w_1 &= p(\Delta V) \\ &= (1 \text{ atm})(40 \text{ L} - 20 \text{ L}) \\ &= 20 \text{ atm-L} \\ &= 20 \times 101.325 \text{ J} \\ &= 2026.5 \text{ J} \end{aligned}$$

$$\text{Process (b)} \quad w_2 = 0, \text{ since the process occurs at constant volume}$$

$$\begin{aligned} \text{Process (c)} \quad w_3 &= nRT \ln \frac{V_2}{V_1} = p_1 V_1 \ln \frac{V_2}{V_1} \\ &= (1 \text{ atm})(20 \text{ L}) \ln (20 \text{ L}/40 \text{ L}) = -13.86 \text{ atm-L} \\ &= -13.86 \times 101.325 \text{ J} = -1404.4 \text{ J} \end{aligned}$$

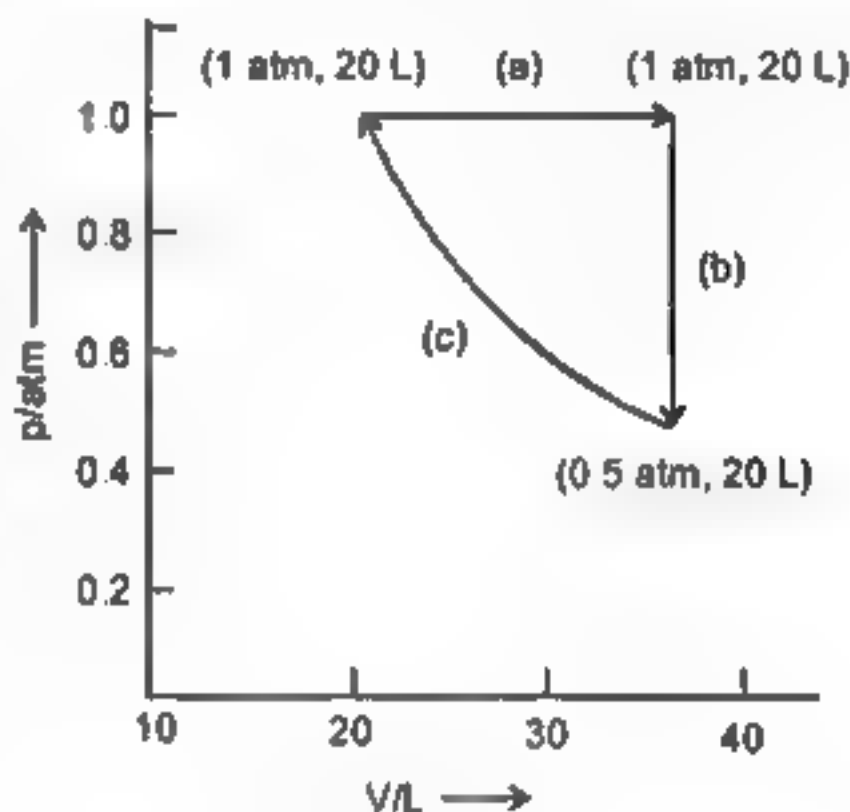
$$\begin{aligned} \text{Total work done, } w &= w_1 + w_2 + w_3 = 2026.5 \text{ J} + 0 - 1404.4 \text{ J} \\ &= 622.1 \text{ J} \end{aligned}$$

Since the given processes constitute a cyclic process, $\Delta U = 0$, and from the first law of thermodynamics, one has

$$q = -w = -622.1 \text{ J}$$

(iii) Since the overall process is a cyclic process,

$$\Delta U = 0 \quad \Delta H = 0 \quad \text{and} \quad \Delta S = 0$$





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29. Calculate the change in energy and enthalpy when 25 litres of argon gas at STP are heated in a cylinder to 110°C . $C_v = \frac{3}{2}R$.
30. One mole of a monoatomic gas at STP undergoes a reversible adiabatic expansion until the volume increases 10 times. Calculate the final pressure and temperature of the gas.
31. Calculate the work done by 3.0 moles of a diatomic gas ($\gamma = 1.40$) at 30°C and 3 atmosphere pressure when it expands adiabatically and reversibly. In the process, its temperature falls to 10°C .
32. Calculate the work done when 5.0 moles of a monoatomic gas ($\gamma = 1.67$) at 35°C and 2 atmosphere pressure is compressed reversibly and adiabatically to final temperature of 45°C .
33. 40 litres of a triatomic gas ($\gamma = 1.33$) at 10 atmosphere undergoes adiabatic expansion to 100 litres at 2 atmosphere. Calculate the decrease in internal energy.
34. 28 g of N_2 ($\gamma = 1.4$) occupying a volume of 20 litres at 1.2 atmosphere expands adiabatically to 80 litres. Calculate the work done by the gas.
35. Calculate work done for the adiabatic expansion of 12 moles of a monoatomic gas ($\gamma = 1.67$) at 27°C and 15 atm to a final pressure of 5 atm.
36. 5 moles of helium gas at -50°C was expanded adiabatically until the temperature fell to -100°C . Calculate the work done by the gas. $\gamma = 1.67$.
37. To what pressure a given volume of fluorine originally at 47°C and 0.5 atm pressure be adiabatically compressed in order to raise its temperature to 87°C . $\frac{C_p}{C_v} = 1.4$.
38. A truck tyre has a pressure of 3 atm at 40°C . If it bursts, find the resulting temperature. $\gamma = 1.4$. The atmospheric pressure is 1.0 atm.
39. 2 g of hydrogen gas at 27°C expands isothermally and reversibly to 100 litres. The work done by the gas is 5744.4 J. What was the initial volume of the gas?
40. The work done when a certain mass of hydrogen gas at 3 atm expand isothermally and reversibly at 50°C to 1 atm is 5900 J. Calculate the mass of hydrogen gas.
41. The heat of combustion of ethylene at 17°C and at constant volume is -1389.9 kJ . Calculate the heat of combustion at constant pressure.
- $$\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$
42. The heat of formation of methane at 25°C at constant pressure is -74852 J . Calculate its heat of formation at constant volume.
- $$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$$
43. The standard enthalpies of formation are $\text{OF}_2(\text{g}) = +23 \text{ kJ mol}^{-1}$, $\text{H}_2\text{O}(\text{g}) = -241.8 \text{ kJ mol}^{-1}$ and $\text{HF}(\text{g}) = -268.6 \text{ kJ mol}^{-1}$. Calculate ΔH° and ΔE° for the reaction:
- $$\text{OF}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{O}_2(\text{g}) + 2\text{HF}(\text{g})$$
44. The energy of reaction for the combustion of *n*-decane is $-6760 \text{ kJ mol}^{-1}$ at 296.3 K .
- $$\text{C}_{10}\text{H}_{22}(\text{l}) + \frac{31}{2} \text{O}_2(\text{g}) \longrightarrow 10\text{CO}_2(\text{g}) + 11\text{H}_2\text{O}(\text{l})$$
- Calculate enthalpy of the reaction at 296.3 K .



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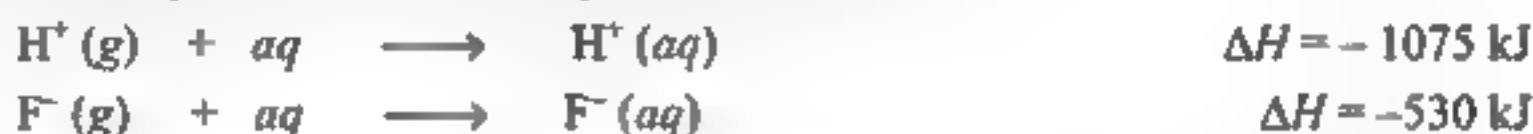


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- 9. Enthalpy of hydration of ions (ΔH_{hyd}).** It is the enthalpy change when 1 mole of gaseous ion is hydrated to form a very dilute solution.



*The enthalpy of hydration for H^+ is taken as 0 by convention.

- 10. Enthalpy of formation of gaseous atoms.** The enthalpy of formation of a gaseous atom is the heat change when 1 mole of gaseous atoms is formed from its element under the standard conditions. For example, enthalpy of formation of oxygen atom is the heat change for the reaction.



Note that the enthalpy of formation of the element, O_2 , is zero but that of oxygen atom is $247.5 \text{ kJ mol}^{-1}$.

- 11. Molar enthalpy of solution (ΔH_s).** It is the heat change when 1 mole of a substance is dissolved in a large excess of the solvent under standard conditions so that further dilution produces no heat change.



- 12. Molar enthalpy of solution and solubility of ionic solids.** For an ionic solid AB,



- (a) The ionic crystal first breaks down to form ions which then get hydrated by water molecules.



$$\text{Enthalpy of solution} = \Delta H_{\text{hyd}} - \text{lattice energy}$$

- 13. Hess's law of constant heat summation.** This law states that heat change in a chemical reaction is the same whether the reaction takes place in one or several stages because the energy of reactants and products depends upon their amounts and final conditions (temperature, pressure, etc.) and not on the history of the reaction.

Explanation. Let the enthalpy change for the conversion of a substance, A, into substance, B, is ΔH . Compound, B, can also be obtained from compound A through the intermediate products C and D for which enthalpy changes are ΔH_1 , ΔH_2 and ΔH_3 respectively.

According to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

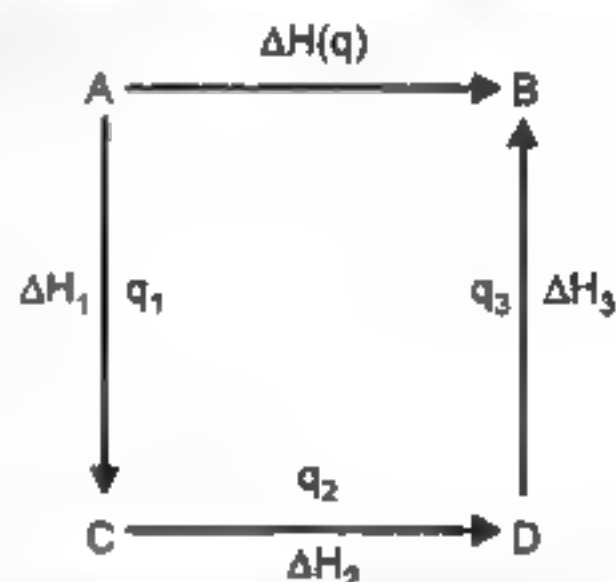


Fig. 19.1 Hess's law of constant heat summation.

- 14. Utility of Hess's law.** It is used for calculating the heat changes for the processes for which direct measurements are not available.
- 15. Thermochemical calculations.** (a) The chemical equations along with enthalpy data are added, subtracted, multiplied or divided in the same manner as for algebraic equations.
- (b) Combine the given chemical equations along with enthalpy data in such a manner that only the desired reactants and products remain.



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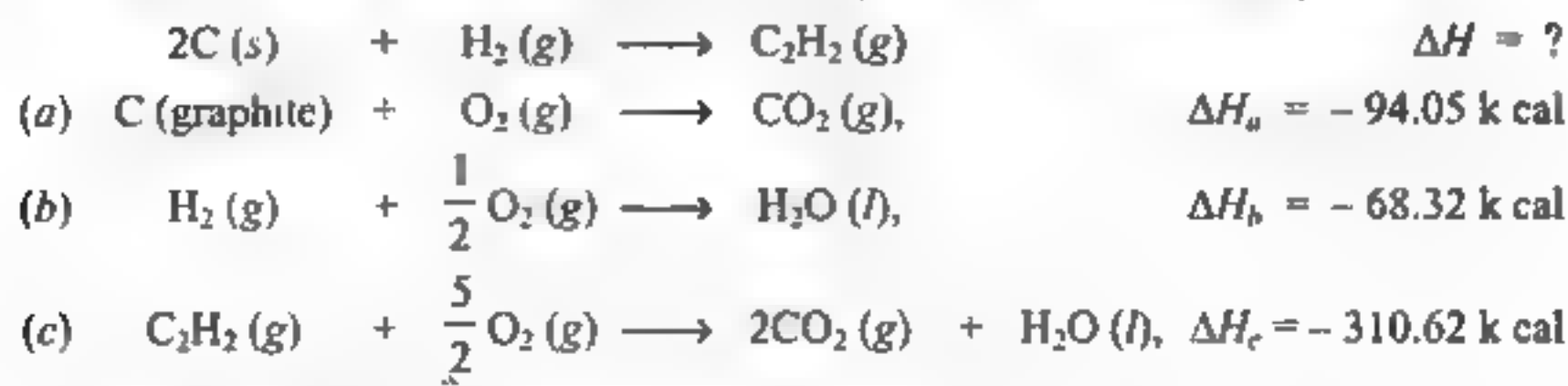


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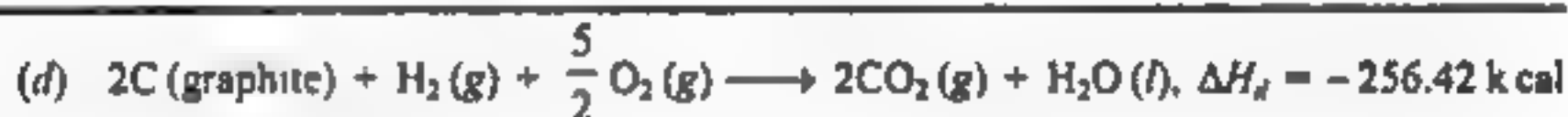
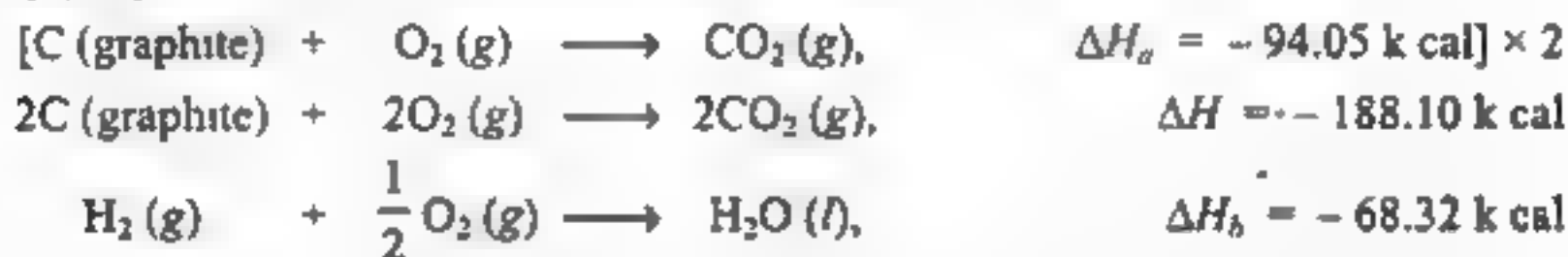


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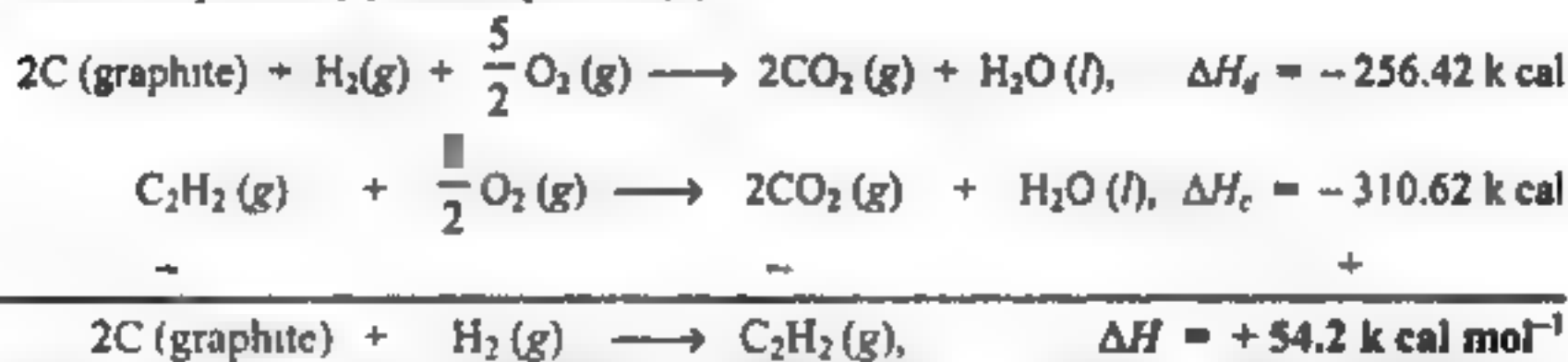
Solution. The heat of formation of C_2H_2 (g) is given by the following equation :



Multiply equation (a) by 2 and then add to equation (b).



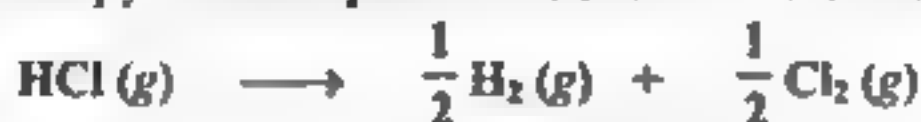
Subtract equation (c) from equation (d).



Problem 23. The enthalpy of formation of solid BaCl_2 is $-860.0 \text{ kJ mol}^{-1}$.



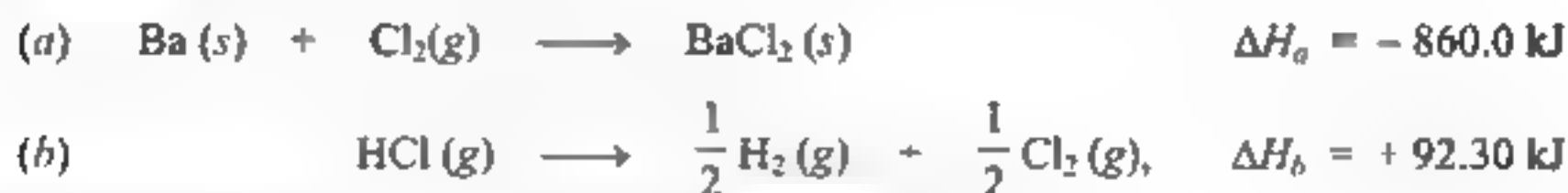
The enthalpy of decomposition of HCl is $+92.30 \text{ kJ mol}^{-1}$.



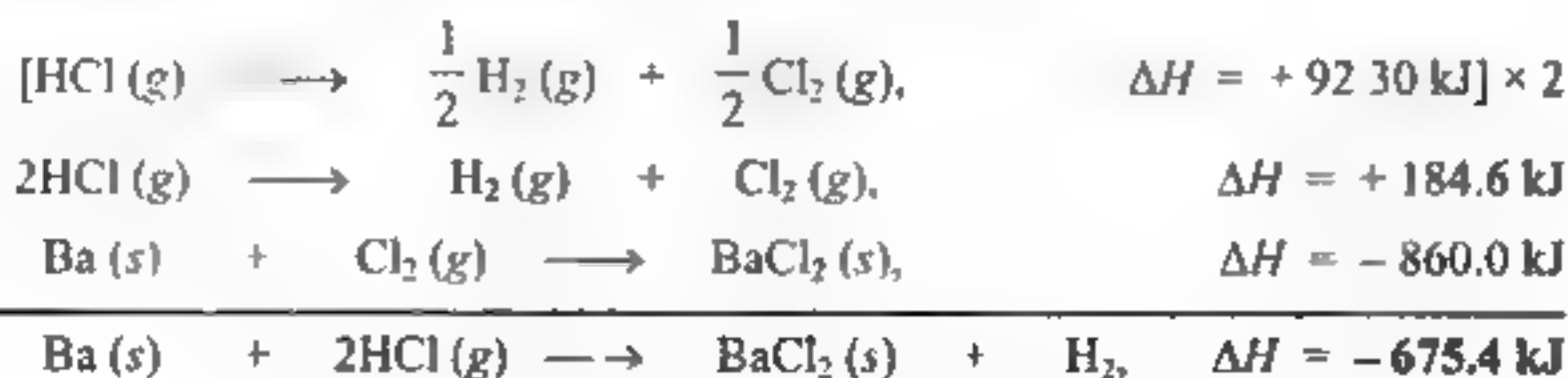
Calculate the enthalpy of the following reaction:



Solution.



Multiply equation (b) by 2 and then add to equation (a).





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$$0.609 \text{ L} = \frac{1 \text{ mol}}{22.4 \text{ L}} \times 0.609 \text{ L} = 0.0272 \text{ mol}$$

$$\text{Volume of methane at } 0^\circ\text{C} = \frac{273 \text{ K}}{298} \times 0.3351 \text{ L} = 0.307 \text{ L}$$

$$22.4 \text{ L} = 1 \text{ mol}$$

$$0.307 \text{ L} = \frac{1 \text{ mol}}{22.4 \text{ L}} \times 0.307 \text{ L} = 0.0137 \text{ mol.}$$

$$\begin{aligned} \text{Amount of heat evolved} &= \text{Moles of ethylene} \times \Delta H_{\text{C}_2\text{H}_4} \times \text{moles of methane} \times \Delta H_{\text{CH}_4} \\ &= 0.0272 \text{ mol} \times (-1423 \text{ kJ mol}^{-1}) + 0.0137 \text{ mol} \times (-891 \text{ kJ mol}^{-1}) \\ &= -38.70 \text{ kJ} - 12.2 \text{ kJ} = -50.9 \text{ kJ} \end{aligned}$$

Problem 32. Determine the enthalpy of the reaction,

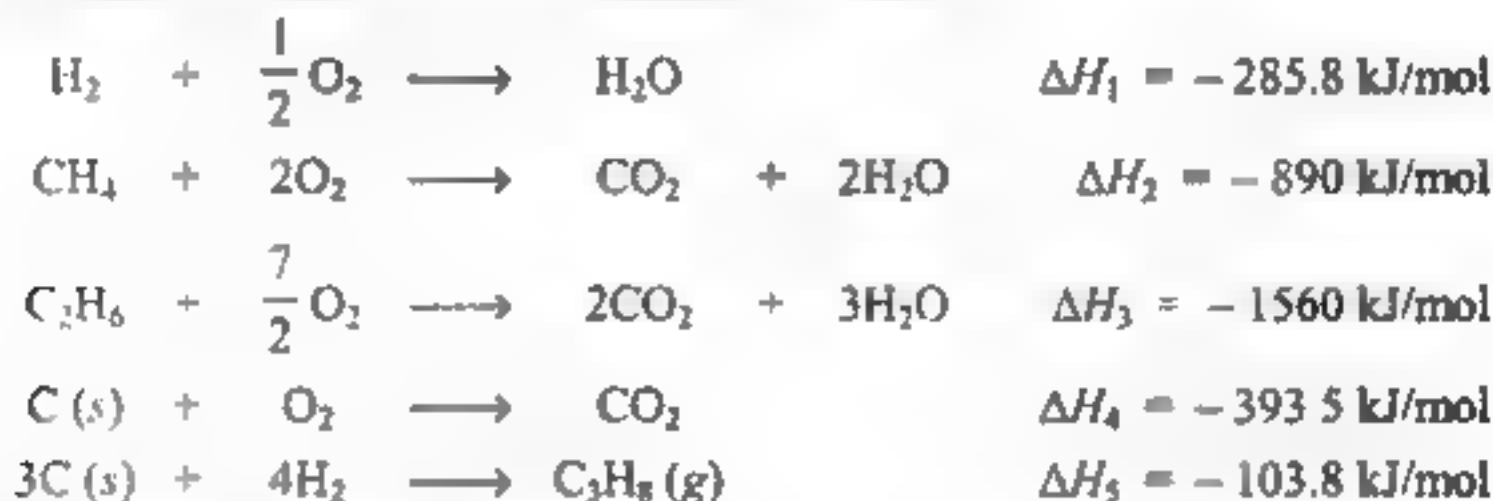


at 25°C using the given heat of combustion values under standard conditions.

| Compound, | $\text{H}_2(\text{g})$, | $\text{CH}_4(\text{g})$, | $\text{C}_2\text{H}_6(\text{g})$, | $\text{C}(\text{graphite})$ |
|----------------------------|--------------------------|---------------------------|------------------------------------|-----------------------------|
| ΔH° (kJ/mol), | -285.8, | -890.0, | -1560.0, | -393.5 |

The standard heat of formation of $\text{C}_3\text{H}_8(\text{g})$ is -103.8 kJ/mol . (IIT/JEE 1992)

Solution. $\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CH}_4(\text{g}) \quad \Delta H = ?$



The required chemical equation is obtained as :

$$\begin{aligned} \Delta H &= 3\Delta H_4 - \Delta H_5 + 5\Delta H_1 - \Delta H_2 - \Delta H_3 \\ &= 3(-393.5) - (-103.8) + 5(-285.8) - (-890) - (-1560) \\ &= -1180.5 + 103.8 - 1429 + 890 + 1560 = -55.7 \text{ kJ/mol.} \end{aligned}$$

Problem 33. 0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of calorimeter system (including water) was found to rise by 0.5°C . Calculate the heat of combustion of methane at (i) constant volume; and (ii) constant pressure. The thermal capacity of the calorimeter system is 17.7 kJ K^{-1} .

(Roorkee 1994)

Solution. Heat liberated during combustion of 0.16 g CH_4 at constant volume

$$\begin{aligned} &= \text{Thermal capacity} \times \text{Rise in temperature} \\ &= 17.7 \text{ kJ K}^{-1} \times 0.5^\circ\text{C} = 8.85 \text{ kJ} \end{aligned}$$

Heat liberated during combustion of 1 mole CH_4

$$= \text{Heat of combustion at constant volume}$$



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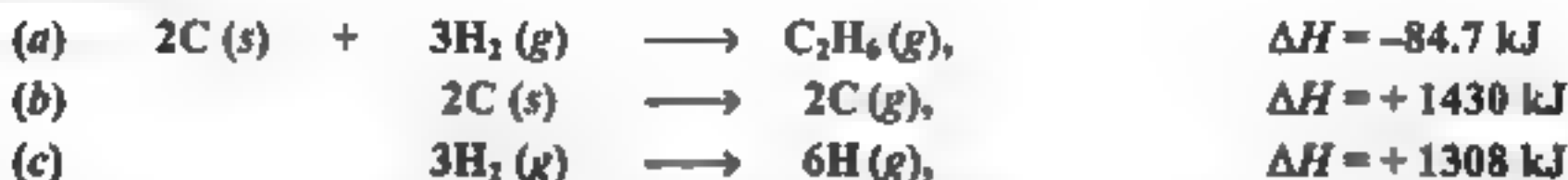
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Calculate the average bond enthalpy (energy) in methane.

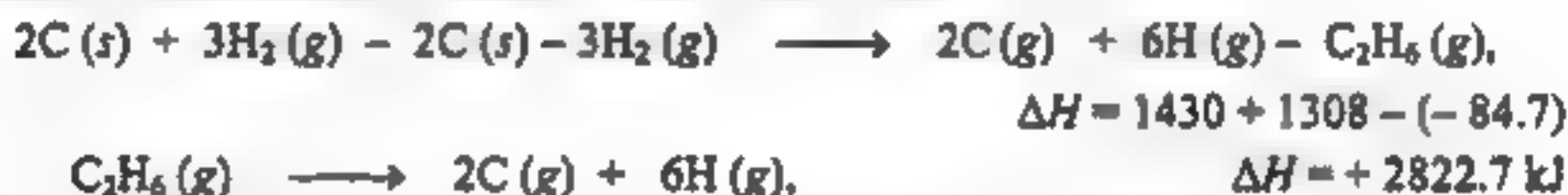
Solution. Average bond energy in methane = $\frac{431 + 364 + 523 + 339}{4}$
 $= \frac{1657}{4} = 414.25 \text{ kJ mol}^{-1}$

Problem 2. Given:



The average bond energy of C – H bond is 413 kJ mol^{-1} . Calculate the single C – C bond energy.

Solution. Subtract eq. (a) from the sum of eq. (b) and eq. (c).



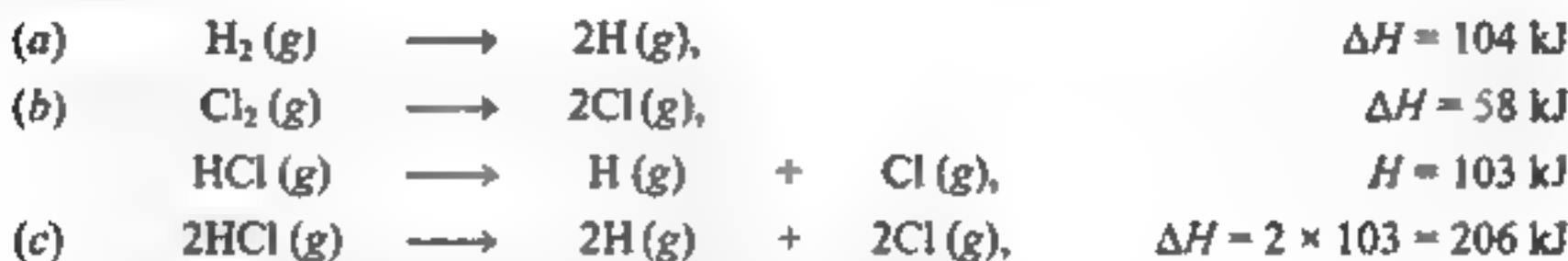
Energy required in breaking 6 moles of C – H bonds in 1 mole of ethane
 $= 6 \times 413 = 2478 \text{ kJ}$

$$\text{Bond energy of single C – C bond} = 2822.7 - 2478 = 344.7 \text{ kJ mol}^{-1}$$

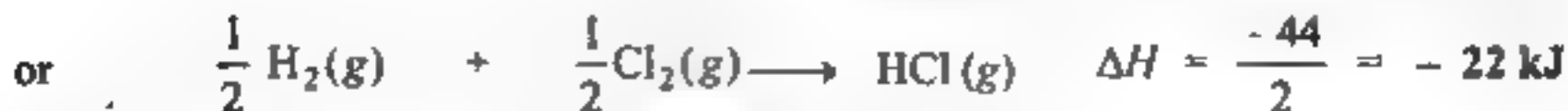
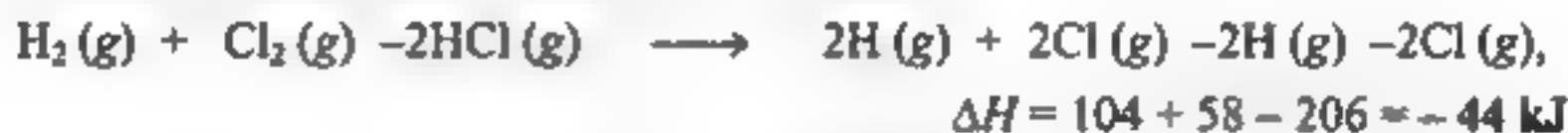
Problem 3. The bond dissociation energies of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 k cal/mol respectively. Calculate the enthalpy of formation of HCl gas.

(IIT/JEE 85)

Solution.

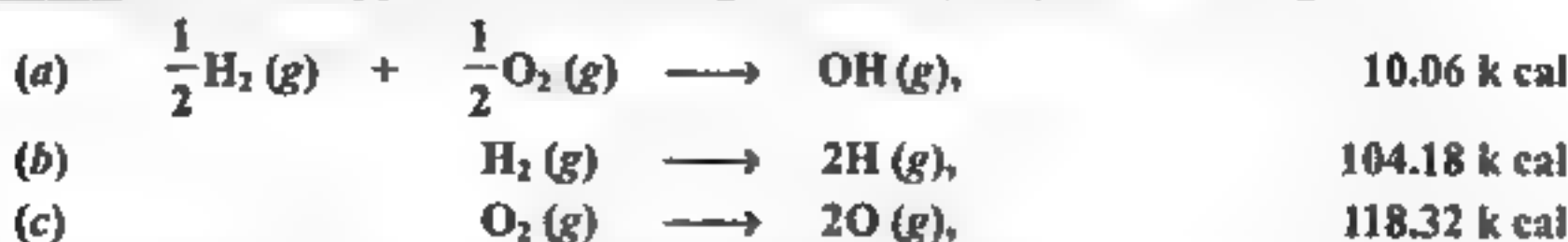


Add eq. (a) and (b) and subtract eq. (c) from the result.



\therefore Enthalpy of formation of HCl gas is -22 kJ mol^{-1} .

Problem 4. The enthalpy for the following reactions (ΔH°) at 25°C are given :



Calculate the O – H bond energy in the hydroxyl radical.

(IIT/JEE 1981)



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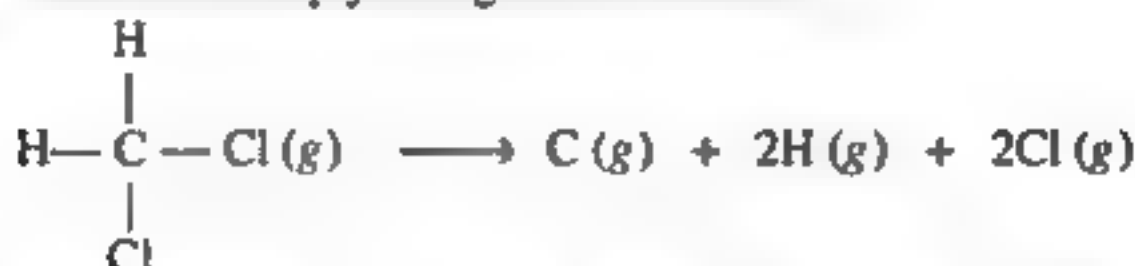
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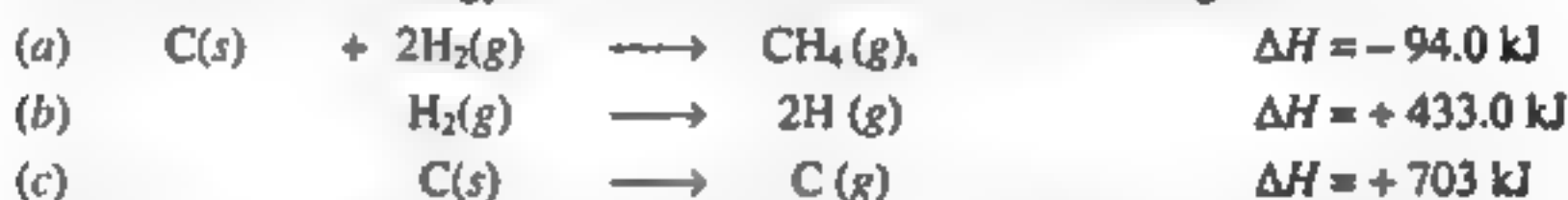
PROBLEMS FOR PRACTICE

1. Calculate enthalpy change for the reaction



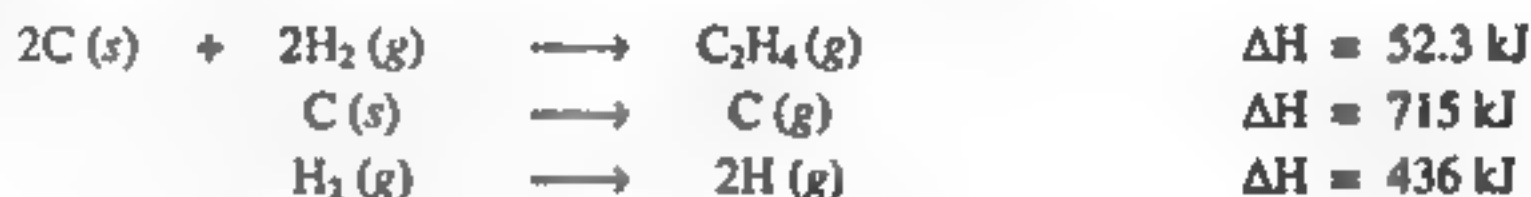
Bond energies for C – H bond and C – Cl bond are 415 kJ and 326 kJ respectively.

2. Calculate the bond energy of the C – H bond from the following data :



3. The bond dissociation energies of gaseous H_2 , F_2 and HF are 435, 155 and 565 kJ mol^{-1} respectively. Calculate the enthalpy of formation of HF gas.

4. Given.



The C – H bond energy is 414 kJ mol^{-1} .

Calculate the C = C bond energy.

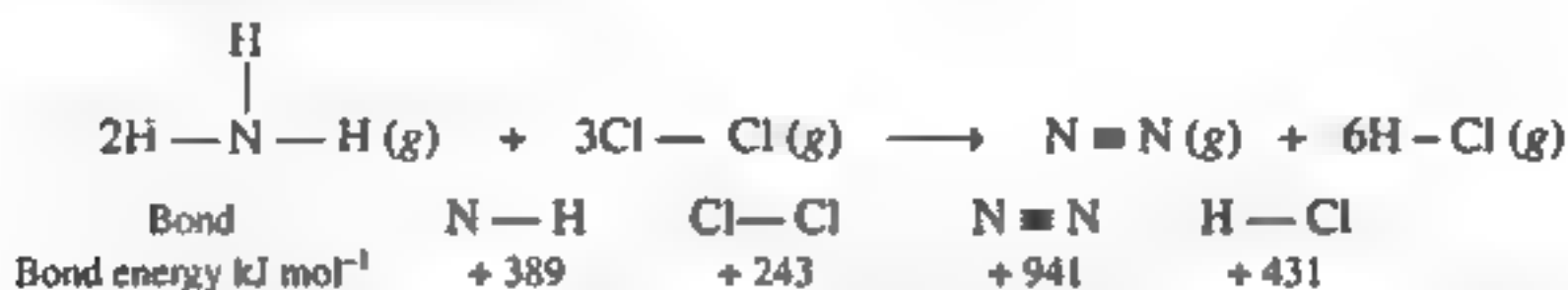
5. The molar enthalpy of formation of benzene (g) is + 83 kJ mol^{-1} . The heats of atomization of carbon and hydrogen are 715 and 436 kJ mol^{-1} respectively. Calculate the C – C bond energy if C – H bond energy is 413 kJ mol^{-1} .



6. Calculate the enthalpy of hydrogenation of ethylene from the following data:

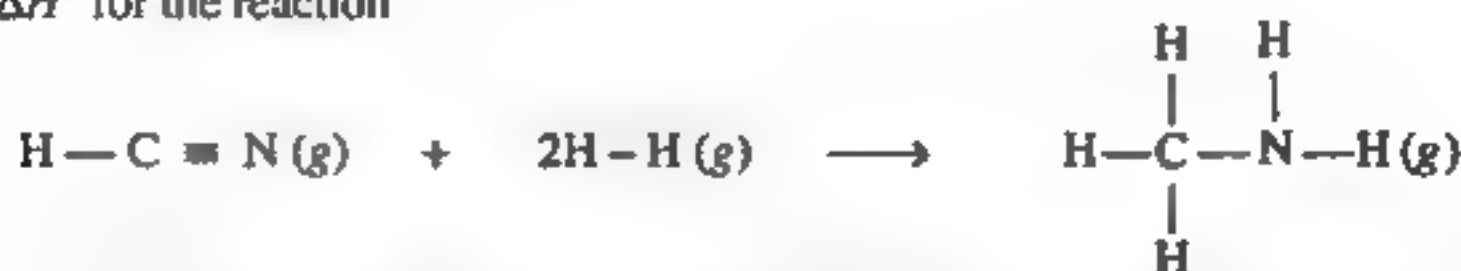
| Bond | C = C | C — C | H — H | C — H |
|----------------------------------|-------|-------|-------|-------|
| Bond energy kJ mol^{-1} | 611 | 346 | 436 | 413 |

7. Calculate ΔH for the reaction



8. The heat of combustion of methane is – 890.4 kJ mol^{-1} . The average bond energies of C — H, O = O and O — H are 413, 494 and 463 kJ mol^{-1} . Calculate the C = O bond energy in carbon dioxide.

9. ΔH° for the reaction



is – 150 kJ. Calculate the bond energy of C ≡ N bond if bond energies of C — H, H — H, C — N and N — H are 414, 435, 293 and 389 kJ mol^{-1} respectively.



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- (c) Its units are J Mole^{-1} or kJ mol^{-1}
- (d) It is a state function.
- (e) It is an extensive property.
- (f) Change in free energy during the process is given as :

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

8. Free energy and useful work. An engine based on heat flow takes heat from a heat source, converts some of it into work and conserves rest of the heat in a cooler region. The energy conserved in a cooler region cannot be converted into work by an engine working in the same temperature range.

$$\therefore \text{Loss of useful work} = T \Delta S.$$

An increase in entropy makes available less energy for doing useful work.

9. Free energy and spontaneous change. Free energy change is a criterion for predicting the spontaneity of a reaction.

For an isothermal change ($T = \text{constant}$),

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ -\Delta G &= -\Delta H + T\Delta S \end{aligned}$$

$$\text{Useful work} = \text{Available energy} - \text{Unavailable energy.}$$

- (i) When ΔG is negative, the reaction occurs spontaneously (favourably).
- (ii) When ΔG is positive, the reaction does not occur but is spontaneous in the reverse direction.
- (iii) When $\Delta G = 0$, the reaction is at equilibrium because the system is not able to do any useful work.

10. Free energy and chemical reactions.

- (a) **Standard free energy (G°)** It is the energy of formation of a substance at 25°C and 1 atmosphere pressure.
- (b) **Standard molar free energy of formation of a compound (ΔG_m°)**. It is defined as the free energy change when 1 mol of the compound is made from its elements in their standard states.



- (c) The standard free energy of formation of an element (at 25°C , 1 atm) is zero by convention, $\text{H}_2 (\text{g})$, $\text{Br}_2 (\text{l})$, $\text{I}_2 (\text{s})$ etc.
- (d) The standard free energy of formation of $\text{H}^+ (\text{aq})$ is zero. The standard free energies of formation for hydrated ions can be calculated using this value.
- (e) **Free energy change in a reaction** = $\frac{\text{Sum of free energies of formation of products}}{\text{Sum of free energies of formation of reactants}}$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$



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(ii) At $T < 463.1$ K, ΔG is positive. Therefore, the forward reaction is non-spontaneous and the backward reaction is spontaneous.

(iii) At $T > 463.1$ K, ΔG is negative. Therefore, the forward reaction is spontaneous.

Problem 4. In the reaction :



there is no entropy change. Enthalpy change, ΔH , equals 50 calories per mole of A^+ . Calculate ΔG for the reaction and comment on the spontaneity of the reaction.

Solution.

$$\Delta S = 0; \quad \Delta H = 50 \text{ cal mol}^{-1}$$

$$\Delta G = \Delta H - T \Delta S = 50 \text{ cal mol}^{-1} - T \times 0 = 50 \text{ cal mol}^{-1}.$$

Since ΔG is positive, the reaction is non-spontaneous.

Problem 5. (a) Calculate the entropy change in 400 kg of water at 55°C when 75 J heat flow out of it into the surroundings at 20°C .

(b) What is the entropy change in the surroundings?

(c) What is the total entropy change in the universe due to this process?

Solution.

$$T_{\text{system}} = 55^\circ\text{C} + 273 = 328 \text{ K}$$

$$T_{\text{surroundings}} = 20^\circ\text{C} + 273 = 293 \text{ K}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= \frac{-q}{T_{\text{system}}} + \frac{+q}{T_{\text{surroundings}}}$$

\therefore Heat flows from the system into surroundings.

$$= -\frac{75 \text{ J}}{328 \text{ K}} + \frac{75 \text{ J}}{293 \text{ K}}$$

$$= -0.2287 + 0.2600 \text{ J K}^{-1} = +0.0313 \text{ J K}^{-1}.$$

Problem 6. 100 joules heat flow from the surroundings at 25°C into a large copper block at -25°C . What is the total entropy change? Assume that the flow of heat does not change the temperature of the copper block and the surroundings.

Solution.

$$T_{\text{system}} = -25^\circ\text{C} + 273 = 248 \text{ K}$$

$$T_{\text{surroundings}} = +25^\circ\text{C} + 273 = 298 \text{ K}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= \frac{+q}{T_{\text{system}}} + \frac{-q}{T_{\text{surroundings}}}$$

\therefore Heat flows from the surroundings into the system.

$$\Delta S_{\text{total}} = \frac{+100 \text{ J}}{248 \text{ K}} + \frac{-100 \text{ J}}{298 \text{ K}}$$

$$= +0.4032 - 0.3356 = +0.0676 \text{ J K}^{-1}.$$

Problem 7. What is the standard entropy for the following reaction:



$$S^\circ_{\text{N}_2} = 191.5 \text{ J K}^{-1} \text{ mol}^{-1}; \quad S^\circ_{\text{NH}_3} = 192.5 \text{ J K}^{-1} \text{ mol}^{-1};$$

$$S^\circ_{\text{H}_2} = 130.59 \text{ J K}^{-1} \text{ mol}^{-1}$$



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Problem 34. The equilibrium constant at 25°C for the process



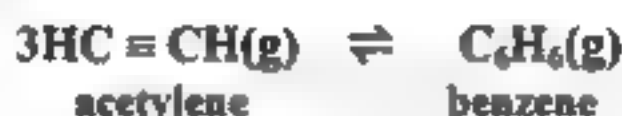
is 2.0×10^7 . Calculate the value of ΔG° at 25°C. $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.

(CBSE 1999 Comptt.)

Solution.

$$\begin{aligned}\Delta G^\circ &= -2.303 RT \log K \\ &= -2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log (2.0 \times 10^7) \\ &= -2.303 \times 8.314 \times 298 \times 7.3010 \\ &= -4.16 \times 10^4 \text{ J mol}^{-1}\end{aligned}$$

Problem 35. (i) Using the data given below, calculate the value of equilibrium constant for the reaction at 298 K : (CBSE 1999)



assuming ideal gas behaviour: $\Delta G_f^\circ, \text{HC} \equiv \text{CH}(\text{g}) = 2.09 \times 10^5 \text{ J mol}^{-1}$;

$\Delta G_f^\circ, \text{C}_6\text{H}_6(\text{g}) = 1.24 \times 10^5 \text{ J mol}^{-1}$; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

(ii) Based on your calculated value, comment whether this process can be recommended as a practical method for making benzene.

Solution. (i)

$$\begin{aligned}\Delta G^\circ &= \Sigma \Delta G_f^\circ, \text{products} - \Sigma \Delta G_f^\circ, \text{reactants} \\ &= \Delta G_f^\circ, \text{C}_6\text{H}_6 - (3 \times \Delta G_f^\circ, \text{CH} \equiv \text{CH}) \\ &= 1.24 \times 10^5 \text{ J mol}^{-1} - (3 \times 2.09 \times 10^5 \text{ J mol}^{-1}) \\ &= -5.03 \times 10^5 \text{ J mol}^{-1}\end{aligned}$$

$$\Delta G^\circ = -2.303 RT \log K$$

$$\log K = \frac{-\Delta G^\circ}{2.303 RT} = \frac{-(-5.03 \times 10^5 \text{ J})}{2.303 \times 8.314 \text{ JK}^{-1} \times 298 \text{ K}}$$

$$K = \text{Antilog } 88.15 = 1.413 \times 10^{88}$$

(ii) Since ΔG° is negative for the above reaction, this process can be recommended for making benzene.

Problem 36. What is the equilibrium constant K for the following reaction at 400 K :



Given, $\Delta H^\circ = 77.2 \text{ kJ mol}^{-1}$, and $\Delta S^\circ = 122 \text{ JK}^{-1} \text{ mol}^{-1}$ at 400 K, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.

Solution.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 77.2 \text{ kJ mol}^{-1} - 400 \text{ K} \times 122 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 77200 \text{ J mol}^{-1} - 48800 \text{ J mol}^{-1} = 28400 \text{ J mol}^{-1}\end{aligned}$$

$$\Delta G^\circ = -2.303 RT \log K$$

$$\log K = \frac{-\Delta G^\circ}{2.303 RT} = \frac{-(-28400 \text{ J mol}^{-1})}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}$$

$$= -3.70 = \bar{4}.30$$

$$K = \text{Antilog } 4.30 = 1.995 \times 10^{-4}$$



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Solution. (i) $\Delta G^\circ_{\text{reaction}} = \Sigma \Delta G_f^\circ, \text{products} - \Sigma \Delta G_f^\circ, \text{reactants}$

$$\begin{aligned} &= \Delta G_f^\circ, \text{CO}_2 - [\Delta G_f^\circ, \text{CO} + \frac{1}{2} \Delta G_f^\circ, \text{O}_2] \\ &= -394.4 - [-137.2 + 0] = -257.2 \text{ kJ} \end{aligned}$$

Since the value of $\Delta G^\circ_{\text{reaction}}$ is negative, the reaction is spontaneous.

(ii) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

or $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = -257.2 \text{ kJ} + (300 \text{ K} \times -0.094 \text{ J mol}^{-1} \text{ K}^{-1})$

$$= -285.4 \text{ kJ mol}^{-1}$$

Since the value of ΔH° is negative, the reaction is exothermic.



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$$\text{Percent by volume} = \frac{\text{Volume of liquid}}{\text{Volume of solution}} \times 100$$

Note that the sum of the percent by volume of all the liquid-components need not be 100. *a* ml of liquid A and *b* ml of liquid B may not give (*a* + *b*) ml of the solution.

- 9. Mole fraction, x .** It is equal to the ratio of the number of moles of the component present to the total number of moles of all the components in the solution.

Mole fraction of a component

$$= \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components in the solution}}$$

If a solution contains '*a*' moles of component A, and '*b*' moles of component B, then

$$\text{Mole fraction of A} = x_A = \frac{a}{a + b}$$

$$\text{Mole fraction of B} = x_B = \frac{b}{a + b}$$

The sum of mole fractions of all the components present in a solution is always equal to one

$$x_A + x_B = \frac{a}{a + b} + \frac{b}{a + b} = 1$$

or

$$x_B = 1 - x_A$$

- 10. Mass fraction.** If W_A is the mass of component A and W_B the mass of component B in a solution, then

$$\text{Mass fraction of A} = \frac{W_A}{W_A + W_B}$$

$$\text{Mass fraction of B} = \frac{W_B}{W_A + W_B}$$

- 11. Parts per million, ppm.** It is a unit to express the concentration in trace amount of a solute in a solution.

$$1 \text{ ppm of a component} = 1 \text{ mg of the component in 1 kg of the solution}$$

$$\text{ppm of A} = \frac{\text{Mass of A}}{\text{Total mass of solution}} \times 10^6$$

- 12. Formality, F .** It is the concentration unit for ionic compounds which dissolve in a polar solvent to give cations and anions. It is the number of gram-formula-weight of the substance dissolved per litre of the solution. It is almost the same as molarity. It describes the solute that is mixed in a liquid rather than the solutes present in solution after the dissolution process.

$$\text{Formality} = F = \frac{\text{Moles of the substance added to the solution}}{\text{Litres of solution}}$$

- 13. Mole percent.** It is the number of moles of a component in 100 moles of the solute and solvent.

$$\text{Mole percent} = \text{Mole fraction} \times 100$$



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$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Litre of solution}}$$

$$6.9 \text{ M} = \frac{0.54 \text{ mol}}{\left(\frac{100/D}{1000}\right) \text{ litre}}$$

or

$$D = \frac{6.9 \times 100}{0.54 \times 1000} = 1.28 \text{ g ml}^{-1}$$

Problem 6. A solution contains 23 g of ethanol and 90 g of water. What is the mole-fraction of ethanol in solution.

Solution. Moles of ethanol = $n_A = \frac{\text{Mass of ethanol}}{\text{Molecular mass of ethanol}}$

$$= \frac{23 \text{ g}}{46 \text{ g/mol}} = 0.5 \text{ mol}$$

Moles of water = $n_B = \frac{\text{Mass of water}}{\text{Molecular mass of water}}$

$$= \frac{90 \text{ g}}{18 \text{ g/mol}} = 5 \text{ mol}$$

$$x_{\text{ethanol}} = \frac{n_A}{n_A + n_B}$$

$$= \frac{0.5 \text{ mol}}{0.5 \text{ mol} + 5 \text{ mol}} = \frac{0.5}{5.5} = 0.09$$

Problem 7. What is the mole fraction of H_2O_2 and H_2O in 20% aqueous hydrogen peroxide?

Solution. 20 g of H_2O_2 is present in 100 g of the solution.

$$\therefore \text{Mass of } \text{H}_2\text{O} \text{ in } 100 \text{ g of } 20\% \text{ } \text{H}_2\text{O}_2 \text{ solution} \\ = 100 - 20 = 80 \text{ g}$$

$$\text{Molecular mass of } \text{H}_2\text{O}_2 = 2 \times 1 + 2 \times 16 = 34 \text{ g/mol}$$

$$\text{Molecular mass of } \text{H}_2\text{O} = 2 \times 1 + 16 = 18 \text{ g/mol}$$

$$\text{Moles of } \text{H}_2\text{O}_2 = \frac{\text{Mass in grams}}{\text{Molecular mass}} = \frac{20 \text{ g}}{34 \text{ g/mol}} = 0.59 \text{ mol}$$

$$\text{Moles of } \text{H}_2\text{O} = \frac{80 \text{ g}}{18 \text{ g/mol}} = 4.44 \text{ mol}$$

$$x_{\text{H}_2\text{O}_2} = \frac{n_{\text{H}_2\text{O}_2}}{n_{\text{H}_2\text{O}_2} + n_{\text{H}_2\text{O}}} = \frac{0.59 \text{ mol}}{0.59 \text{ mol} + 4.44 \text{ mol}} = 0.117$$

$$x_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}_2} + n_{\text{H}_2\text{O}}} = \frac{4.44 \text{ mol}}{0.59 \text{ mol} + 4.44 \text{ mol}} = 0.883$$

or

$$x_{\text{H}_2\text{O}} = 1 - x_{\text{H}_2\text{O}_2} = 1 - 0.117 = 0.883$$



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Problem 18. What volume of 95% sulphuric acid (density = 1.85 g/mL) and what mass of water must be taken to prepare 100 mL of 15% solution of H_2SO_4 (density = 1.10 g/mL)? (CBSE 1989)

Solution. 95 g H_2SO_4 is present in 100 g of sulphuric acid solution.

$$\text{Volume of 100 g of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ g}}{1.85 \text{ g/mL}} = 54.05 \text{ mL}$$

15 g H_2SO_4 is present in 100 g of sulphuric acid.

$$\text{Volume of 100 g of 15% } \text{H}_2\text{SO}_4 \text{ solution} = \frac{100 \text{ g}}{1.10 \text{ g/mL}} = 90.9 \text{ mL}$$

\therefore 90.9 mL solution contains 15 g H_2SO_4

$$100 \text{ mL solution contains } \frac{15 \text{ g}}{90.9 \text{ mL}} \times 100 \text{ mL} = 16.5 \text{ g } \text{H}_2\text{SO}_4$$

95 g H_2SO_4 is present in (95%) 54.05 mL of solution

$$16.5 \text{ g } \text{H}_2\text{SO}_4 \text{ is present in } \frac{54.05 \text{ mL}}{95 \text{ g}} \times 16.5 \text{ g} = 9.39 \text{ mL (95% } \text{H}_2\text{SO}_4)$$

\therefore Volume of 95% H_2SO_4 required = 9.39 mL

$$\text{Volume of water required} = 100 \text{ mL} - 9.39 \text{ mL}$$

$$= 90.61 \text{ mL } \text{H}_2\text{O} = 90.61 \text{ g } \text{H}_2\text{O}$$

Problem 19. How many moles of naphthalene are present in 2 litres of 0.05 M naphthalene dissolved in benzene?

$$\text{Solution.} \quad \text{Molarity} = \frac{\text{Moles of Naphthalene}}{\text{Volume of solution in litres}}$$

$$\begin{aligned} \text{Moles of naphthalene} &= \text{Molarity} \times \text{Volume of solution in litres} \\ &= 0.05 \text{ M} \times 2 \text{ litres} = 0.1 \text{ mol} \end{aligned}$$

Problem 20. The density of 85% phosphoric acid is 1.70 g/cm³.

(i) What is the molarity of the solution?

(ii) What volume of the acid has to be used to make 1 litre of 0.2 M H_3PO_4 ?

Solution. 85 g phosphoric acid is present in 100 g of the solution.

$$\text{Volume of 100 g of the acid} = \frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ g}}{1.70 \text{ g/cm}^3} = 58.8 \text{ cm}^3$$

$$\begin{aligned} \text{Molecular mass of } \text{H}_3\text{PO}_4 &= 3 \times \text{amu H} + \text{amu P} + 4 \times \text{amu O} \\ &= 3 \times 1 + 31 + 4 \times 16 = 98 \text{ g/mol.} \end{aligned}$$

$$\text{Moles of phosphoric acid} = \frac{\text{Mass of the solute (H}_3\text{PO}_4)}{\text{Molecular mass of H}_3\text{PO}_4}$$

$$= \frac{85 \text{ g}}{98 \text{ g/mol}} = 0.867 \text{ mol.}$$

$$\begin{aligned} \text{(i)} \quad \text{Molarity} &= \frac{\text{Moles of solute}}{\text{Volume of solution in litres}} = \frac{0.867 \text{ mol}}{(58.8/1000) \text{ L}} \\ &= 14.75 \text{ M} \end{aligned}$$



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$$\frac{\text{Molarity}}{\text{Molality}} = \frac{\text{Density of solution} \times \text{Volume of solution} - \text{Mole of solute} \times \text{Molecular mass of solute}}{\text{Volume of solution in litres}}$$

$$\frac{11.5}{94.5} = \frac{(d \times 1000 - 1 \times 98)}{1000}$$

$$11.5 \times 1000 = 94.5 (1000d - 98)$$

$$11500 = 94500d - 9261$$

$$94500d = 20761$$

$$\text{or } d = 0.218 \text{ gm/cc}$$

Problem 28. When one litre of 0.5 M HCl is heated in a beaker, its volume reduced to 600 mL and 1.825 g HCl was lost as vapour. Calculate the molarity of the resulting solution.

$$\text{Solution. Moles of HCl lost} = \frac{\text{Mass of HCl}}{\text{Molecular mass of HCl}} = \frac{1.825 \text{ g}}{36.5 \text{ g/mol}} = 0.05 \text{ mol}$$

$$\begin{aligned} \text{Number of moles of HCl present in the resulting 600 mL solution} &= \text{Moles of HCl initially present} - \text{Moles of HCl lost} \\ &= 0.5 \text{ mol} - 0.05 \text{ mol} = 0.45 \text{ mol} \end{aligned}$$

$$\begin{aligned} \therefore \text{Molarity of the resulting solution} &= \frac{\text{Moles of HCl present}}{\text{Volume of HCl solution in litres}} \\ &= \frac{0.45 \text{ mol}}{(600/1000) \text{ L}} = 0.75 \text{ M} \end{aligned}$$

Problem 29. Calculate the mass percentage of a solution obtained by mixing 100 g of 10% urea solution with 150 g of 15% urea solution.

$$\text{Solution. Mass of urea in 100 g solution 10\% solution} = 10 \text{ g}$$

$$\text{Mass of urea in 150 g solution of 15\% solution} = \frac{15}{100} \times 150 = 22.5 \text{ g}$$

$$\begin{aligned} \text{Total mass of urea in (100 g + 150 g)} &= 250 \text{ g solution)} \\ &= 10 \text{ g} + 22.5 \text{ g} = 32.5 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Mass \% urea after mixing the solutions} &= \frac{\text{Mass of urea}}{\text{Mass of solution}} \times 100 \\ &= \frac{32.5 \text{ g}}{250 \text{ g}} \times 100 = 13\%. \end{aligned}$$

Problem 30. A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Calculate (i) molal concentration and (ii) mole fraction of sugar in the syrup.

(IIT/JEE 1988)

$$\text{Solution. (a) Mass of sugar syrup} = 214.2 \text{ g}$$

$$\text{Mass of sugar} = 34.2 \text{ g}$$

$$\text{Mass of water} = 214.2 \text{ g} - 34.2 \text{ g} = 180.0 \text{ g}$$

$$\text{Molecular mass of sugar} = 12 \times 12 + 22 \times 1 + 11 \times 16 = 342 \text{ g/mol}$$

$$\text{Moles of sugar, } n_A = \frac{\text{Mass of sugar}}{\text{Molecular mass of sugar}}$$



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$$= \frac{45 \times 0.25}{1000} \text{ mol} = 0.01125 \text{ mol}$$

Millimoles of chromic sulphate in 25 mL solution = 25 mL \times 0.10 M

$$= \frac{25 \times 0.10}{1000} = 0.0025 \text{ mL}$$



$$\text{Moles of sulphate formed} = 3 \text{ mol} \times 0.0025 \text{ mol} = 0.0075 \text{ mol}$$

\therefore Moles of lead sulphate formed = 0.0075 mol

$$(i) \quad \text{Moles of Pb}^{2+} \text{ left} = 0.01125 \text{ mol} - 0.0075 \text{ mol} = 0.00375 \text{ mol}$$

$$\begin{aligned} \text{Molarity of Pb}^{2+} \text{ left} &= \frac{\text{Moles} \times 1000 \text{ mL}}{\text{Volume in mL}} \\ &= \frac{0.00375 \text{ mol} \times 1000 \text{ mL}}{70 \text{ mL}} = 0.05357 \text{ M} \end{aligned}$$

$$(ii) \quad \text{Moles of NO}_3^- \text{ left} = 4 \times 0.01125 \text{ mol} = 0.02250 \text{ mol}$$

$$\text{Molarity of NO}_3^- = \frac{0.02250 \text{ mol}}{70 \text{ mL}} \times 1000 \text{ mL} = 0.3214 \text{ M}$$

$$(iii) \quad \text{Moles of Cr}^{3+} \text{ left} = 2 \times 0.0025 \text{ mol} = 0.005$$

$$\text{Molarity of Cr}^{3+} = \frac{0.005 \text{ mol} \times 1000 \text{ mL}}{70 \text{ mL}} = 0.0714 \text{ M}$$

Problem 33. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm³ of a solution of density 1077.2 kg m⁻³. Calculate the molality, molarity and mole fraction of Na₂SO₄ in the solution. (IIT/JEE 1994)

Solution. (a) Molecular mass of Glauber's salt, Na₂SO₄·10H₂O

$$= 2 \times 23 + 32 + 4 \times 16 + 10 \times 18 = 332 \text{ g/mol}$$

$$\text{Mass of Glauber's salt} = 8.0575 \times 10^{-2} \text{ kg} = 80.575 \text{ g}$$

$$\text{Moles of Glauber's salt} = \frac{\text{Mass}}{\text{Molecular mass}} = \frac{80.575 \text{ g}}{332 \text{ g/mol}} = 0.25 \text{ mol}$$

$$\text{Volume of solution} = 1 \text{ dm}^3 = 1 \text{ L}$$

$$\text{Molarity} = \frac{0.25 \text{ mol}}{1 \text{ L}} = 0.25 \text{ M}$$

$$(b) \quad \text{Density} = 1077.2 \text{ kg m}^{-3} = 1077.2 \text{ g dm}^{-3}$$

$$\text{Mass of 1 dm}^3 \text{ of solution} = \text{Volume} \times \text{Density}$$

$$= 1 \text{ dm}^3 \times 1077.2 \text{ g dm}^{-3} = 1077.2 \text{ g}$$

$$\text{Mass of water} = 1077.2 \text{ g} - 80.575 \text{ g} = 996.625 \text{ g}$$

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{0.25 \text{ mol}}{(996.625/1000) \text{ kg}} = 0.2508 \text{ m}$$



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$$p_A = p_A^\circ \times x_A \quad \dots(i)$$

If x_B is the mole-fraction of the non-volatile solute B, then

$$x_A + x_B = 1$$

or

$$x_A = 1 - x_B \quad \dots(ii)$$

Substituting the value of x_A from eq. (ii) into eq. (i), one obtains

$$p_A = p_A^\circ \times (1 - x_B) = p_A^\circ - p_A^\circ x_B$$

$$\boxed{\frac{p_A^\circ - p_A}{p_A^\circ} = x_B} \quad \dots(iii)$$

Therefore, Raoult's law states that the relative lowering of vapour-pressure ($p_A^\circ - p_A$) / p_A° for a non-volatile solute is equal to the mole fraction of the solute.

5. Ideal solution. Mixing of two substances results in an ideal solution only when

- (i) it obeys Raoult's law over all concentration ranges,
- (ii) ΔH mixing is zero, i.e., no heat is absorbed or released during dissolution.
- (iii) ΔV mixing is zero, i.e., the total volume of the solution is equal to the sum of the volumes of the pure components mixed to form a solution.

6. Non-ideal solution. A solution which does not obey Raoult's law over all concentration ranges is called a non-ideal solution. It forms with a change in volume and enthalpy. The plot of the total vapour-pressure of the components versus mole fraction is not a straight line but a curve with a positive or negative deviation.

7. Positive deviation from Raoult's law. In such a solution of two liquids A and B, the attraction between molecules of A and molecules of B is less than that between A - A molecules or between B - B molecules and ΔH is positive. It forms an azeotrope with minimum boiling point and maximum vapour-pressure.

8. Negative deviation from Raoult's law. In such a solution of two liquids A and B, the attraction between molecules of A and B is greater than that between A - A molecules or B - B molecules and ΔH is negative. It forms an azeotrope with a maximum boiling point and minimum vapour-pressure.

9. Distillation and azeotropes. On heating a solution of two liquids at the boiling point, the vapour contains more of the volatile component. If heating is continued certain systems form constant-boiling mixtures called azeotropes. The composition of the vapour is equal to that of the constant boiling azeotrope and therefore no more separation of the liquids is possible by distillation.

10. Relation between mole fraction of a substance in the vapour to the mole fraction of liquid and vapour-pressure of the pure liquid. For a solution of two miscible liquids A and B :

$$\text{Mole-fraction of A in the vapour} = x_A(v) = \frac{p_A}{p_{\text{Total}}}$$

where p_A is the partial vapour-pressure of the gaseous component A and p_{Total} is the total vapour-pressure of all the gaseous components.

$$p_A = p_A^\circ x_A(l)$$

$$\boxed{x_A(v) = \frac{x_A(l) p_A^\circ}{p_{\text{Total}}}}$$



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Volume of the vapour = Volume of dry oxygen passed
= 100 litre

Using the gas equation, $pV = nRT$

$$\begin{aligned} p &= \frac{nRT}{V} \\ &= \frac{(3.18 \text{ g} / 74 \text{ g/mol}) (0.082 \text{ lit-atm K}^{-1} \text{ mol}^{-1}) (298 \text{ K})}{100 \text{ litre}} \\ &= 0.0105 \text{ atm} \\ &= 0.0105 \text{ atm} \times \frac{760 \text{ mm}}{1 \text{ atm}} = 7.9 \text{ mm Hg.} \end{aligned}$$

Problem 11. The vapour-pressure of pure water at 30°C is 31.50 mm Hg. When 3.0 g of a non-volatile solute was dissolved in 54 g of water, the vapour-pressure of the solution was found to be 31.30 mm Hg. Calculate the molar mass of the solute.

(CBSE 1989C)

Solution. $P^\circ_A = 31.50 \text{ mm}$, $P_A = 31.30 \text{ mm}$, $W_B = 3.0 \text{ g}$, $W_A = 54 \text{ g}$, $M_B = ?$
 $M_A = 2 \times 1 + 16 = 18 \text{ g/mol}$

$$\frac{P^\circ_A - P_A}{P^\circ_A} = x_B = \frac{W_B / M_B}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

or
$$\frac{31.50 \text{ mm} - 31.30 \text{ mm}}{31.50 \text{ mm}} = \frac{3 / M_B}{\frac{54}{18} + \frac{3}{M_B}}$$

$$\frac{0.20}{31.50} = \frac{(3 / M_B) \times (18 M_B)}{54 M_B + 18 \times 3} = \frac{54}{54 M_B + 54} = \frac{1}{M_B + 1}$$

$$0.20 (M_B + 1) = 31.50 \times 1$$

$$0.20 M_B + 0.20 = 31.50$$

$$0.20 M_B = 31.50 - 0.20 = 31.30$$

$$M_B = \frac{31.30}{0.20} = 156.5 \text{ g/mol}$$

Problem 12. Two liquids X and Y on mixing form an ideal solution. At 30°C , the vapour-pressure of the solution containing 3 mol of X and 1 mol of Y is 550 mm Hg. But when 4 mol of X and 1 mol of Y are mixed, the vapour-pressure of the solution thus formed is 560 mm Hg. What would be the vapour pressure of pure X and Y at this temperature?

(CBSE 1996)

Solution. $P_X = P^\circ_X x_X = P^\circ_X \times \frac{n_X}{n_X + n_Y}$; $P_Y = P^\circ_Y x_Y = P^\circ_Y \times \frac{n_Y}{n_X + n_Y}$

(i) For a solution containing 3 mol of X and 1 mol of Y

$$P_{\text{Total}} = P_X + P_Y = P^\circ_X \times \left(\frac{3 \text{ mol}}{3 \text{ mol} + 1 \text{ mol}} \right) + P^\circ_Y \times \left(\frac{1 \text{ mol}}{3 \text{ mol} + 1 \text{ mol}} \right)$$



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$$P = \frac{\frac{100 \text{ g}}{18 \text{ g}}}{\frac{100 \text{ g}}{18 \text{ g}} + \frac{W}{60}}$$

$$\frac{3}{4} P^\circ = P^\circ \times \frac{\frac{100 \text{ g}}{18 \text{ g}}}{\frac{100 \times 60 + 18 W}{18 \times 60}} = \frac{100}{18} \times \frac{18 \times 60}{6000 + 18 W}$$

$$6000 + 18 W = 6000 \times \frac{4}{3} = 8000$$

$$18 W = 8000 - 6000 = 2000$$

$$W = \frac{2000}{18} = 111.1 \text{ g urea}$$

$$\begin{aligned} \text{Molality of urea solution} &= \frac{\text{Moles of urea}}{\text{Mass of water in kg}} \\ &= \frac{111.1 \text{ g} / 60 \text{ g mol}^{-1}}{100 \text{ g}} \times (1000 \text{ g/kg}) = 18.52 \text{ m.} \end{aligned}$$

Problem 19. The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density = 0.867 g mL^{-1}) increases by a factor of 7720 at 20°C . A solution of benzene and toluene at 20°C has a vapour-pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution. (IIT/JEE 1996)

Solution. Molecular mass of benzene = 78 g/mol

Mass of 1 mole of benzene = 78 g

$$\text{Volume of 1 mole of benzene} = \frac{\text{Mass}}{D} = \frac{78 \text{ g/mol}}{0.877 \text{ g/mL}} = 88.94 \text{ mL}$$

$$\text{Volume of benzene in the gaseous phase} = 2750 \times \frac{88.94 \text{ mL}}{1000 \text{ mL/L}} = 244.58 \text{ L}$$

Molecular mass of toluene = 92 g/mol

$$\text{Volume of 1 mole of liquid toluene} = \frac{92 \text{ g/mol}}{0.867 \text{ g/mL}} = 106.11 \text{ mL}$$

$$\text{Volume of 1 mole of gaseous toluene} = 7720 \times \frac{106.11 \text{ mL}}{1000 \text{ mL/L}} = 819.19 \text{ L}$$

$$PV = nRT \quad \text{or} \quad P = \frac{nRT}{V}$$

$$P_{(\text{Benzene})}^\circ = \frac{1 \text{ mol} \times 0.082 \text{ L-atm K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}{244.58 \text{ L}} = 0.098 \text{ atm}$$

$$P_{(\text{Toluene})}^\circ = \frac{1 \text{ mol} \times 0.082 \text{ L-atm K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}{819.19 \text{ L}} = 0.029 \text{ atm}$$



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Colligative Properties

- 1. Lowering of vapour pressure and boiling-point elevation.** A liquid boils at a temperature when its vapour pressure becomes equal to external pressure. A solution has a lower vapour pressure than the pure solvent and so boils at a higher temperature where the vapour pressure becomes equal to external pressure. The boiling point elevation of a dilute solution is proportional to the molality of the solute.

$$\Delta T_b = T_b - T_b^\circ = K_b m$$

where, T_b° and T_b are the boiling points of the pure solvent and solution respectively, ΔT_b is elevation of boiling point and m is the solute molality K_b is a constant known as ebullioscopic constant or molal boiling point elevation constant of the solvent.

- 2. Ebullioscopic constant of a solvent.** It is equal to the boiling point elevation when 1 kg of the solvent contains 1 mole of the solute particles (1 m). It depends upon the number of particles of the solute in solution and not on its nature (identity). *1 mole of any solute causes the same increase in boiling point of the solvent.*
- 3. Lowering the vapour pressure and Freezing point depression.** A liquid solidifies at a temperature when the vapour pressure of the liquid and solid are same. Addition of a solute decreases the vapour pressure of the pure liquid. Therefore, for a solid to have the same vapour pressure as that of the solution, the freezing point should lower down.

A solution has a lower freezing point than the pure solvent and depression of freezing point of dilute solution is proportional to the solute molality.

$$\Delta T_f = T_f^\circ - T_f = K_f m$$

where, T_f° and T_f are the freezing points of pure solvent and solution respectively and K_f is the cryoscopic constant or molal freezing point depression constant of the solvent and m is the molality of the solute.

- 4. Cryoscopic constant of a solvent.** It is equal to the freezing point depression when 1 kg of solvent contains 1 mole of the solute (1 m) particles. It depends upon the number of particles of the solute in solution and not on its nature (identity). *1 mole of any solute causes the same decrease in freezing point of the solvent.*
- 5. Determination of molecular mass of a solute.** Measurement of boiling point elevation or freezing point depression using Beckmann thermometer affords a convenient method for the determination of the molecular masses of the solutes. In fact, it is a method of determining the number of moles of the solute particles present in the solution.

(a) Using boiling point elevation

$$\Delta T_b = K_b m = \frac{K_b \times W_2 \text{ g} \times 1000 \text{ g/kg}}{M_2 \text{ g/mol } W_1 \text{ g}}$$



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Problem 4. What is the boiling point of an aqueous solution containing 0.6 g urea and 0.9 g glucose in 100 g water. K_b of water is 0.52 K/m.

Solution. Mass of urea in 1000 g water = $0.6 \text{ g} \times \frac{1000 \text{ g}}{100 \text{ g}} = 6 \text{ g}$

Mass of glucose in 1000 g water = $0.9 \text{ g} \times \frac{1000 \text{ g}}{100 \text{ g}} = 9 \text{ g}$

Molecular mass of urea, $\text{NH}_2\text{CONH}_2 = 60 \text{ g/mol}$

Molecular mass of glucose, $\text{C}_6\text{H}_{12}\text{O}_6 = 180 \text{ g/mol}$

Moles of urea = $\frac{6 \text{ g}}{60 \text{ g/mol}} = 0.1 \text{ mol}$

Moles of glucose = $\frac{9 \text{ g}}{180 \text{ g/mol}} = 0.05 \text{ mol}$

Total molality = $0.1 \text{ m} + 0.05 \text{ m} = 0.15 \text{ m}$

$\Delta T_b = T_b - T_b^\circ = 0.52 \text{ K/m} \times 0.15 \text{ m} = 0.078$

$T_b = 100^\circ\text{C} + 0.078^\circ\text{C} = 100.078^\circ\text{C}.$

OR
$$\Delta T_b = K_b \times \frac{W_B}{M_B} \times \frac{1000}{W_A} = \frac{0.52 \times 0.1 \times 1000}{60 \times 100} = 0.078 \text{ K}$$

$\Delta T_b = T_b - T_b^\circ$ or $0.078 = T_b - 373 \text{ K}$

or $T_b = 373 + 0.078 = 373.078 \text{ K}$

Problem 5. A solution of 4.2 g of a non-volatile solute in 50 g of acetone boils at 57.8°C . What is the molecular mass of the solute? Boiling point and K_f of pure acetone are 56°C and 1.71 K/m respectively.

Solution. Mass of solute in 50 g acetone = 4.2 g

$\Delta T_b = 57.8 - 56 = 1.8^\circ\text{C}$

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000$$

$$= \frac{1.71 \text{ K/m}}{1.8 \text{ K}} \times \frac{4.2 \text{ g}}{50 \text{ g}} \times 1000 \text{ g/kg} = 80 \text{ g/mol}$$

Problem 6. A 4.8% erythritol aqueous solution freezes at -0.772°C . What is the molecular mass of erythritol? K_f of water is 1.86°C/m .

Solution. Mass of erythritol, $W_2 = 4.8 \text{ g}$

Mass of water $W_1 = 100 - 4.8 = 95.2 \text{ g}$

$\Delta T_f = 0^\circ\text{C} - (-0.772^\circ\text{C}) = 0.772^\circ\text{C}$

$$M_2 = \frac{K_f}{\Delta T_f} \times \frac{W_2}{W_1} \times 1000 \text{ g/kg}$$

$$= \frac{1.86 \text{ K/m}}{0.772 \text{ K}} \times \frac{4.8 \text{ g}}{95.2 \text{ g}} \times 1000 \text{ g/kg} = 121.5 \text{ g/mol}.$$



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Final volume of the solution = 150 mL + 150 mL = 300 mL

Total number of moles of solutes in solution = 0.0167 mol + 0.0088 mol = 0.0255 mol

$$\pi V = nRT$$

$$\pi = \frac{nRT}{V}$$

$$= \frac{0.0255 \text{ mol} \times 0.082 \text{ L-atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{300/1000 \text{ litres}}$$

$$= 2.09 \text{ atm}$$

Problem 16. On dissolving 3.24 g of sulphur in 40 g of benzene boiling point of solution was higher than that of benzene by 0.81 K. K_b value of benzene is 2.53 K kg mol⁻¹. What is the molecular formula of sulphur? (Atomic mass of sulphur = 32 g mol⁻¹). (CBSE 2000)

Solution.

$$M_{\text{solute}} = \frac{K_b \times W_{\text{solute}} \times 1000}{\Delta T_b \times W_{\text{solvent}}} = \frac{2.53 \text{ K m}^{-1} \times 3.24 \text{ g} \times 1000}{0.81 \text{ K} \times 40 \text{ g}}$$

$$= 253 \text{ g/mol}$$

Atomic mass of sulphur = 32 g/mol

Molecular mass of S_x = 253 g/mol

$$x \times 32 \text{ g/mol} = 253 \text{ g/mol}$$

$$x = \frac{253}{32} = 7.9 \approx 8$$

Therefore, molecular formula of sulphur is S₈.

Problem 17. An aqueous solution freezes at 272.4 K, while pure water freezes at 273.0 K. Determine: (i) the molality of solution; (ii) boiling point of solution; (iii) lowering of vapour pressure of water at 298 K. (Given: $K_f = 1.86 \text{ K kg mol}^{-1}$; $K_b = 0.512 \text{ K kg mol}^{-1}$ and vapour pressure of water at 298 K = 23.756 mm Hg) (CBSE 1998)

Solution.

$$\Delta T_f = 273.0 \text{ K} - 272.4 \text{ K} = 0.6 \text{ K}$$

(i) $\Delta T_f = K_f \cdot m$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.6 \text{ K}}{1.86 \text{ K kg mol}^{-1}} = 0.322 \text{ m}$$

(ii) $\Delta T_b = K_b \times m$

$$T_b - T_b^\circ = 0.512 \text{ K kg mol}^{-1} \times 0.322 \text{ m} = 0.165 \text{ K}$$

$$T_b = T_b^\circ + 0.165 \text{ K} = 373 \text{ K} + 0.165 \text{ K} = 373.165$$

(iii) Mole-fraction of the solute = Molality \times Molar mass of the solvent in kg

$$= 0.322 \text{ m} \times \frac{18}{1000} \text{ kg} = 0.0057$$

$$\frac{P_A^\circ - P_A}{P_A^\circ} = x_B$$

$$P_A^\circ - P_A = x_B P_A^\circ$$

$$= 0.0057 \times 23.756 \text{ mm} = 0.135 \text{ mm}$$



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Abnormal Molecular Masses and Van't Hoff Factor

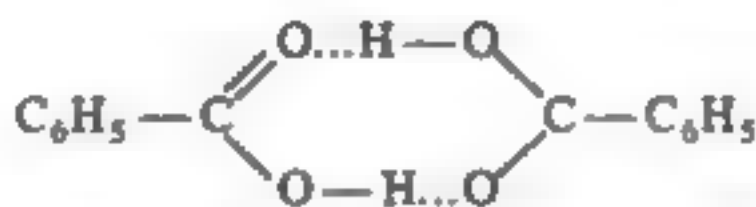
1. **Colligative property.** Lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure are colligative properties. They depend on the number of solute particles in solution and not on their identity.

Colligative property \propto Number of solute particles in solution

2. **Abnormal molecular mass.** The molecular mass calculated using a colligative property is abnormal if the solute dissociates or associates in solution.
3. **The extent of dissociation.** A solute that dissociates *completely or partially* in solution makes available more particles than would otherwise be present and, therefore, a colligative property shows an increased effect. For example, molecular masses obtained from strong electrolytes as solutes such as strong acids, bases and salts are much less than their normal values. As an example, one particle of potassium chloride on dissociation in water gives two particles, K^+ and Cl^- and, therefore, the molecular mass obtained by a colligative property is half of its normal molecular mass.



4. **The extent of association.** A solute that associates in solution provides less particles than would otherwise be present and, therefore, the colligative property shows the decreased effect. For example, benzoic acid in benzene is found to have a molecular mass which is just twice its normal molecular mass.



A dimer of benzoic acid

It is found that compounds which are capable of forming hydrogen bonds, e.g., phenols, carboxylic acids, alcohols etc. associate and so show decreased effect of colligative property.

5. In general

$$\begin{aligned} (a) \quad & \frac{\text{Colligative property expected theoretically}}{\text{Colligative property observed experimentally}} \\ &= \frac{\text{Moles of solute dissolved}}{\text{Moles of solute actually present after dissociation or association}} \\ &= \frac{\text{Molality}}{\text{Effective Molality}} \end{aligned}$$

$$(b) \quad \frac{\text{Normal Molecular mass}}{\text{Observed Molecular mass}} = i = \text{Van't Hoff factor}$$



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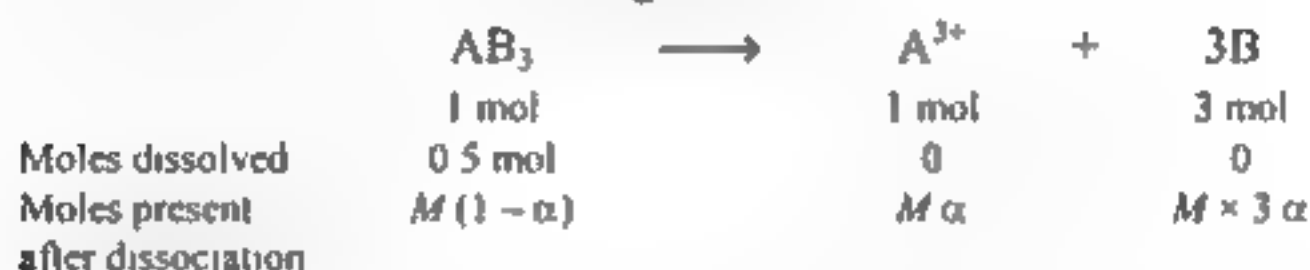
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$$\begin{aligned}
 0.0832 &= 0.0312(1 + 2\alpha) \\
 \text{or} \quad 1 + 2\alpha &= \frac{0.0832}{0.0312} = 2.67 \\
 2\alpha &= 2.67 - 1 = 1.67 \\
 \alpha &= \frac{1.67}{2} = 0.835
 \end{aligned}$$

Problem 5. The osmotic pressure of a solution containing 85 g per litre of AB_3 (molecular mass 170) in water is 40 atm at 27°C . What is the degree of dissociation of AB_3 ?

Solution. Mass of AB_3 = 85 g per litre

$$\text{Molarity of } \text{AB}_3 \text{ solution} = \frac{85 \text{ g/litre}}{170 \text{ g/mol}} = 0.5 \text{ M}$$



$$\begin{aligned}
 \text{Total Molarity} &= M(1 - \alpha) + M\alpha + 3M\alpha \\
 &= M[(1 - \alpha + \alpha + 3\alpha)] = M(1 + 3\alpha) = 0.5(1 + 3\alpha)
 \end{aligned}$$

$$\pi V = nRT$$

$$40 \text{ atm} \times 1 \text{ litre} = 0.5(1 + 3\alpha) \times 0.082 \text{ lit-atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$

$$1 + 3\alpha = \frac{40}{0.5 \times 0.082 \times 300} = 3.253$$

$$3\alpha = 3.253 - 1 = 2.253$$

$$\alpha = \frac{2.253}{3} = 0.751$$

$$\text{Percent dissociation} = 0.751 \times 100 = 75.1\%$$

Problem 6. Benzoic acid in benzene associates to form a dimer $(\text{C}_6\text{H}_5\text{COOH})_2$. A solution containing 6.1 g benzoic acid in 500 g benzene lowered the freezing point by 0.2898 degrees. What is the Van't Hoff factor and the degree of association of benzoic acid in benzene? K_f for benzene is 5.52 K/m.

Solution. Normal molecular mass of benzoic acid, $\text{C}_6\text{H}_5\text{COOH} = 122 \text{ g mol}^{-1}$

$$\begin{aligned}
 \text{Observed molecular mass of benzoic acid} &= \frac{K_f}{\Delta T_f} \times \frac{W_2}{W_1} \times 1000 \\
 &= \frac{5.52 \text{ K/m}}{0.2898 \text{ K}} \times \frac{6.1 \text{ g} \times 1000 \text{ g/kg}}{500 \text{ g}} = 232.4 \text{ g mol}^{-1}
 \end{aligned}$$

$$\text{Van't Hoff factor, } i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} = \frac{122 \text{ g/mol}}{232.4 \text{ g/mol}} = 0.5680$$

For association of benzoic acid, 2 molecules associate to give 1 molecule, therefore

$$n = 2$$



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$$m \left(1 - \alpha + \frac{\alpha}{2} \right) = m \left(1 - \frac{\alpha}{2} \right)$$

$$\Delta T_f = K_f m (\text{effective})$$

$$0.69 \text{ K} = 5.12 \text{ K m} \times \left[\frac{20}{94} \left(1 - \frac{\alpha}{2} \right) \right] m$$

$$1 - \frac{\alpha}{2} = \frac{0.69 \times 94}{5.12 \times 20} = 0.6334$$

$$\frac{\alpha}{2} = 1 - 0.6334 = 0.3666$$

$$\alpha = 2 \times 0.3666 = 0.7332 \approx 0.73$$

Problem 13. 2.0 g of benzoic acid dissolved in 25.0 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant (K_f) of benzene is 4.9 K kg mol⁻¹. What is the percentage association of the acid? (Roorkee 1990)

Solution. Molality of benzoic acid before association

$$\frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{2.0 \text{ g} / 122 \text{ g mol}^{-1}}{(25/1000) \text{ kg}}$$

$$= \frac{2.0}{122} \times \frac{1000}{25} = 0.656 \text{ m}$$

| | | | |
|---------------------------------|------------------------------------|-------------------|---------------------------------------|
| | $2\text{C}_6\text{H}_5\text{COOH}$ | \longrightarrow | $(\text{C}_6\text{H}_5\text{COOH})_2$ |
| Moles dissolved | m | | 0 |
| Moles present after association | $m(1 - \alpha)$ | | $\frac{m\alpha}{2}$ |

$$\text{Total number of effective moles} = m(1 - \alpha) + m \frac{\alpha}{2}$$

$$= m \left(1 - \alpha + \frac{\alpha}{2} \right) = m \left(1 - \frac{\alpha}{2} \right)$$

$$\text{Total number of effective moles} = 0.656 \left(1 - \frac{\alpha}{2} \right)$$

$$\Delta T_f = K_f m (\text{effective})$$

$$1.62 \text{ K} = 4.9 \text{ K m}^{-1} \times 0.656 \left(1 - \frac{\alpha}{2} \right) m$$

$$1 - \frac{\alpha}{2} = \frac{1.62}{4.9 \times 0.656} = 0.504$$

$$\frac{\alpha}{2} = 1 - 0.504 = 0.496$$

$$\alpha = 2 \times 0.496 = 0.992$$

Problem 14. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300 K. Calculate the osmotic pressure of the solution. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

(Roorkee 1991)



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PROBLEMS FOR PRACTICE

1. A weak electrolyte AB is 12% dissociated in aqueous solution. What is the freezing point of a 0.100 molal aqueous solution of AB? K_f for water is 1.86 K/m.
2. A 0.1 molal of acetic acid is 1.34% ionized. What is the boiling point of this solution? K_b for water is 0.52 K/m.
3. The freezing point of a 0.5 molal KBr solution is -1.66°C . What is the degree of dissociation of KBr? K_f for water is 1.86 K/m.
4. The freezing point of an aqueous solution of potassium sulphate, K_2SO_4 , containing 3.48 g of the salt in 100 g water is -1.10°C . What is the Van't Hoff factor and degree of dissociation of K_2SO_4 ? K_f for water is 1.86 K/m.
5. A_3B is 25% dissociated in aqueous solution. What is the boiling point of a 0.3 molal aqueous solution? K_b for water is 0.52 K/m.
6. What is the osmotic pressure of a solution containing 8.2 g calcium nitrate in 500 ml solution at 300 K? The degree of dissociation of calcium sulphate at this dilution is 0.91.
7. The osmotic pressure of a 0.119% KBr solution is 0.4594 atm at 40°C . What is the degree of dissociation and Van't Hoff factor of KBr?
8. Acetic acid associates in benzene to form a dimer. A solution containing 6 g acetic acid in 250 g benzene raised the boiling point by 0.516°C . What is the Van't Hoff factor and the degree of association of acetic acid in benzene. K_b for benzene is 2.53 K/m.
9. Three particles of a solution, A, associate in benzene to give a species A_3 . The freezing point of a 0.25 molal solution in benzene is 4.74°C . What is the degree of association of the solute in solution? Freezing point and K_f for benzene are 5.5°C and 5.12 K/m.
10. One-tenth of a mole of sugar was dissolved in a kg of water. Depression in freezing point was determined to be 0.186 K. What conclusion can you draw about its molecular state? K_f for water is $1.8 \text{ K mol}^{-1} \text{ per kg}$. (CBSE 1985)
11. The freezing point depression of a 0.1 m AB solution is 0.372°C . What conclusion can you draw about its molecular state? K_f for water is $1.86 \text{ K mol}^{-1} \text{ deg}^{-1}$.
12. The freezing point depression of a 0.1 m acetic acid in benzene is 0.256 K. What conclusion can you draw about the state of the solute in solution? K_f for benzene is 5.12 K/m. (CBSE 1982)
13. A 0.0103 M solution of potassium sulphate is found to have an osmotic pressure of 0.680 atmosphere at 299 K. Calculate the value of i for the solution.
14. A solution of 1.20 g of MgSO_4 in 100 g of water has a boiling point 0.06292 K higher than pure water. Calculate the Van't Hoff factor for the solution. The ebullioscopic-constant of water is 0.52 K/m.
15. A solution contains 5.85 g of an electrolyte in 180 g of water. Its vapour pressure is found to be 348.6 mm Hg at 80°C . The vapour pressure of pure water is 355.1 mm Hg at 80°C . Molecular mass of the electrolyte is 58.5 g/mol. Calculate the Van't Hoff factor of the solution.

ANSWERS

- | | | | |
|----------------------------|---------------------------------------|-----------------------|-----------------------|
| 1. -0.21°C | 2. 100.0527°C | 3. 0.79 | 4. (i) 2.96 (ii) 0.98 |
| 5. 100.273°C | 6. 3.47 atm | 7. (i) 0.79 (ii) 1.79 | 8. (i) 0.51 (ii) 0.98 |
| 9. 0.66 | 10. no association no dissociation | 11. 2, dissociation | 12. 0.5, association |
| 13. 2.69 | 14. 1.21 | 15. 1.87 | |



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which concentration of a reactant is reduced to *one-half* of the initial concentration and is written as $t_{1/2}$.

(a) $\text{rate} = k[A]$

$$\boxed{-\frac{d[A]}{dt} = k[A]}$$

where $[A]$ is the concentration of the reactant, A, at time t and k is the rate constant of the reaction.

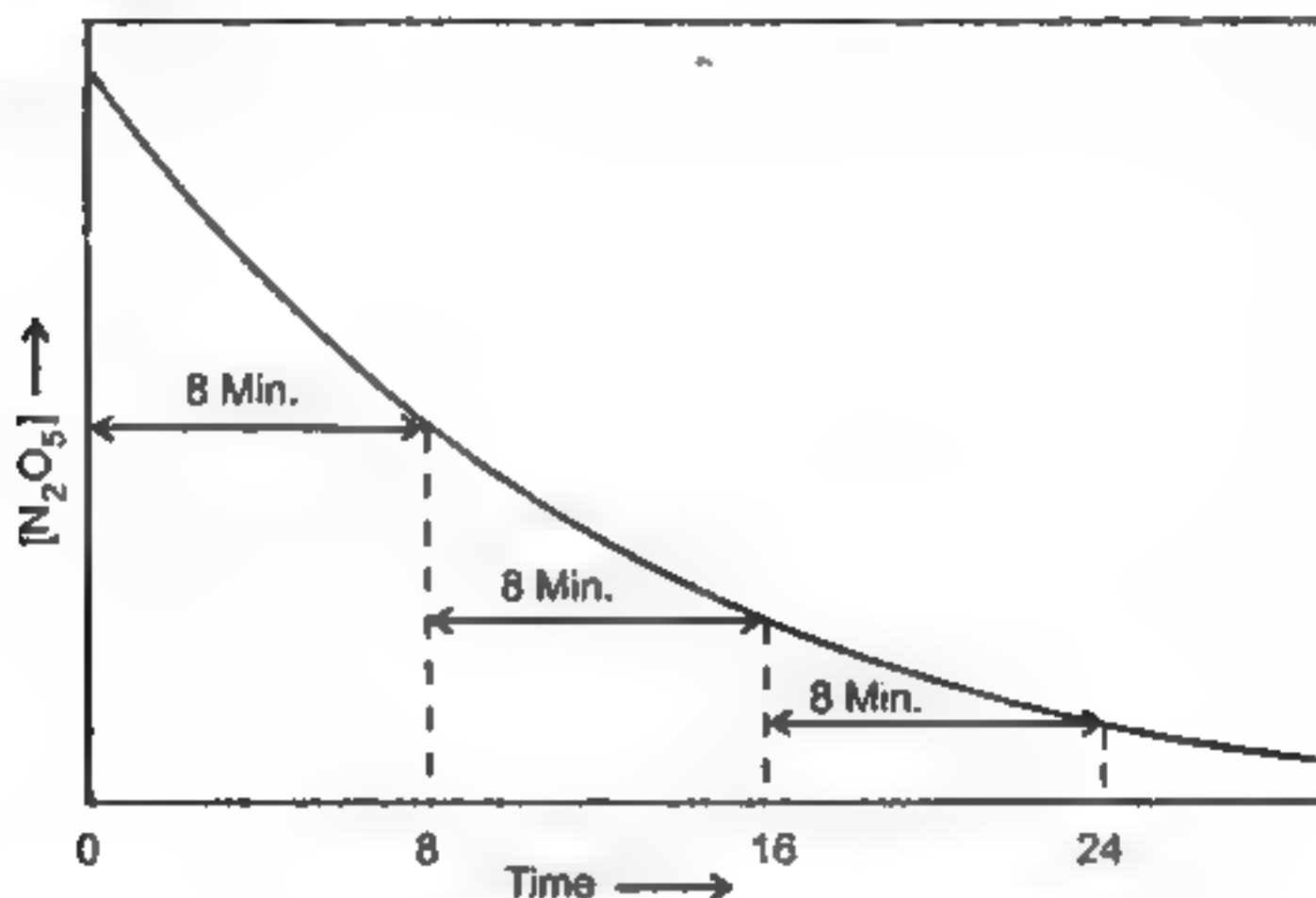


Fig. 26.1 Half life for a first order reaction

(b) Integration of the rate law gives :

$$2.303 \log_{10} \frac{\text{Initial concentration}}{\text{Concentration at time } t} = kt$$

$$\log_{10} \frac{C_0}{C_t} = \frac{kt}{2.303}$$

where, C_t is the concentration of A at time t and C_0 is the initial concentration.

or
$$\log_{10} \frac{C_2}{C_1} = -\frac{k(t_2 - t_1)}{2.303}$$

where, C_1 is the concentration of A at time t_1 and C_2 is the concentration of A at time t_2 .

(c)
$$k = \frac{2.303}{t} \log_{10} \frac{\text{Initial concentration}}{\text{concentration at time } t}$$

$$= \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

where, a is the initial concentration of the reactant. x is the concentration that has reacted in time t and k is the rate constant of the reaction.

8. Half-life of a reaction. The half-life of a first order reaction is independent of the initial concentration of the reactant.



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$$9 \propto [3]^b$$

$$3^2 \propto [3]^b$$

$$\therefore b = 2$$

The order w.r.t. reactant, NO, is 2.

(b) Rate expression: $\text{Rate} \propto k [\text{Cl}_2] [\text{NO}]^2$

where k is rate constant of the reaction

$$(c) \quad k = \frac{\text{Rate}}{[\text{Cl}_2] [\text{NO}]^2} = \frac{1 \times 10^{-3}}{(0.05) \times (0.05)^2} = 8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

$$(d) \quad \begin{aligned} \text{Rate} &= k [\text{Cl}_2] [\text{NO}]^2 \\ &= 8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} \times (0.2 \text{ M}) \times (0.4 \text{ M})^2 \\ &= 0.256 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Problem 17. From the following data for the reaction between A and B,

| [A] | [B] | Initial rate mol lit ⁻¹ s ⁻¹ , at | |
|----------------------|----------------------|---|----------------------|
| | | 300 K | 320 K |
| 2.5×10^{-4} | 3.0×10^{-5} | 5.0×10^{-4} | 2.0×10^{-3} |
| 5.0×10^{-4} | 6.0×10^{-6} | 4.0×10^{-3} | — |
| 1.0×10^{-3} | 6.0×10^{-6} | 1.6×10^{-2} | — |

calculate :

- the order of the reaction with respect to A and with respect to B,
- the rate constant at 300 K,
- the energy of activation, and
- the pre-exponential factor.

Solution. (i) Let the order w.r.t. reactant A be x and the order w.r.t. reactant B be y

$$\begin{aligned} \therefore \text{Rate law} &= k [\text{A}]^x [\text{B}]^y \\ 5.0 \times 10^{-4} &= k [2.5 \times 10^{-4}]^x [3.0 \times 10^{-5}]^y & \dots(i) \\ 4.0 \times 10^{-3} &= k [5.0 \times 10^{-4}]^x [6.0 \times 10^{-5}]^y & \dots(ii) \\ 1.6 \times 10^{-2} &= k [1.0 \times 10^{-3}]^x [6.0 \times 10^{-5}]^y & \dots(iii) \end{aligned}$$

Dividing eqn. (iii) by eqn. (ii),

$$\frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}} = \frac{k [1.0 \times 10^{-3}]^x \times [6.0 \times 10^{-5}]^y}{k [5.0 \times 10^{-4}]^x \times [6.0 \times 10^{-5}]^y}$$

$$4 = 2^x$$

$$2^2 = 2^x$$

$$\text{or} \quad x = 2$$

Dividing eqn. (ii) by eqn. (i), one has

$$\frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \frac{k [5.0 \times 10^{-4}]^x \times [6.0 \times 10^{-5}]^y}{k [2.5 \times 10^{-4}]^x \times [3.0 \times 10^{-5}]^y}$$

$$8 = 2^x \times 2^y = 2^{x+y}$$

$$\text{or} \quad = 2^3 = 2^{x+y}$$



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From the slow step, one can write

$$-\frac{d[O_2]}{dt} = k_2[N_2O_2][O_2] \quad \dots(i)$$

Since, the first step is in rapid equilibrium, one can write

$$K_{eq} = \frac{[N_2O_2]}{[NO]^2} \quad \dots(ii)$$

Putting the value of $[N_2O_2]$ from eq (ii) into eq (i), one has

$$-\frac{d[O_2]}{dt} = (k_2K_{eq})[NO]^2[O_2]$$

k_2 increases with increase in temperature but K_{eq} decreases with increase in temperature. As K_{eq} outweighs k_2 , the rate constant k decreases with increase in temperature.

Problem 21. For the reaction,



the following initial rates were obtained at various given initial concentrations

| S.No. | [A] | [B] | Rate ($\text{mol L}^{-1} \text{sec}^{-1}$) |
|-------|-----|-----|--|
| 1. | 0.1 | 0.1 | 0.05 |
| 2. | 0.2 | 0.1 | 0.10 |
| 3. | 0.1 | 0.2 | 0.05 |

Write rate law and find the rate constant of the above reaction. (IIT Mains 2004)

Solution. When

$$[B] = 0.1$$

$$R_1 = 0.05 = (0.1)^a$$

$$R_2 = 0.10 = (0.2)^a$$

$$\frac{0.10}{0.05} = \frac{(0.2)^a}{(0.1)^a} = 2^a \quad \text{or } a = 1$$

When

$$[A] = 0.1 \quad R = 0.05 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$R_1 = 0.05 = (0.1)^b$$

$$R_2 = 0.05 = (0.2)^b$$

\therefore

$$b = 0$$

So the reaction is first order with respect to A and zero order with respect to B

\therefore

$$\text{Rate} = k[A]^1[B]^0 = k[A]$$

or

$$k = \frac{\text{Rate}}{[A]} = \frac{0.05 \text{ mol L}^{-1} \text{ s}^{-1}}{0.1 \text{ mol L}^{-1}} = 5 \times 10^{-1} \text{ s}^{-1}$$



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$$\begin{aligned}
 \text{(i)} \quad t_{1/2} \text{ or } t_{50\%} &= \frac{2.303}{k} \log \frac{1}{1-0.5} = \frac{2.303}{k} \log 2 \\
 \text{(ii)} \quad t_{1/3} &= \frac{2.303}{k} \log \frac{1}{1-1/3} = \frac{2.303}{k} \log \frac{3}{2} \\
 \text{(iii)} \quad t_{2/3} &= \frac{2.303}{k} \log \frac{1}{1-2/3} = \frac{2.303}{k} \log 3
 \end{aligned}$$

Table 27.1 Units of rate constant for first, second, third and zero order reactions.

| S. No. | Order of reaction | Differential rate | Integrated rate law | Units of k |
|--------|-------------------|-----------------------------|--|--|
| 1. | First | $\frac{-d[A]}{dt} = k[A]$ | $k = -\frac{1}{[A]} \cdot \frac{d[A]}{dt}$ | sec^{-1} |
| 2. | Second | $\frac{-d[A]}{dt} = k[A]^2$ | $k = -\frac{1}{[A]^2} \cdot \frac{d[A]}{dt}$ | $\text{litre mol}^{-1} \text{sec}^{-1}$ or $\text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}$ |
| 3. | Third | $\frac{-d[A]}{dt} = k[A]^3$ | $k = -\frac{1}{[A]^3} \cdot \frac{d[A]}{dt}$ | $\text{litre}^2 \text{mol}^{-2} \text{sec}^{-1}$ or $\text{dm}^6 \text{mol}^{-2} \text{sec}^{-1}$ |
| 4. | Zero | $\frac{-d[A]}{dt} = k_0$ | $k_0 = -\frac{a_0 - a}{dt}$ | $\text{mol litre}^{-1} \text{sec}^{-1}$ |

8. A plot of $\log [\text{concentration}]$ of the reactant *versus* time gives a straight line with slope equal to $-k/2.303$.

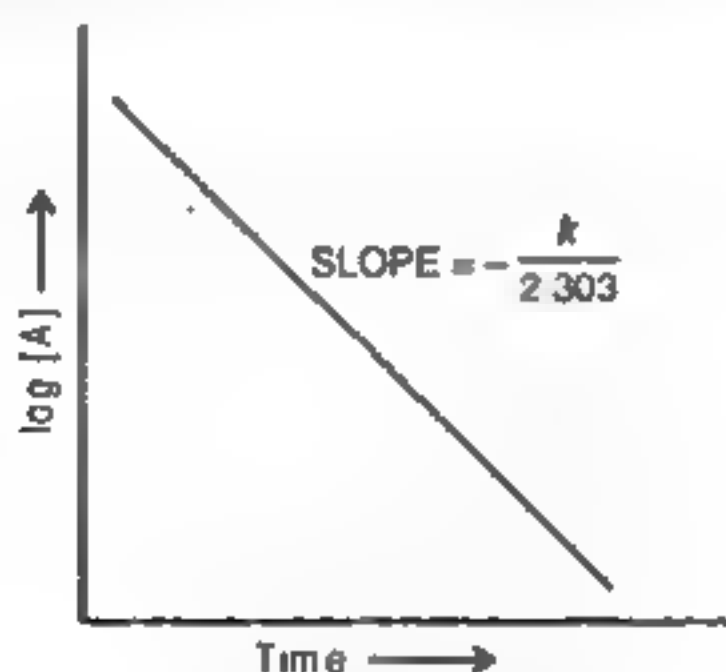


Fig. 27.1.

9. Chemical kinetics and concentrations of reactants and products expressed in terms of pressures.

(a) Dalton's law of partial pressures

$$P_T = p_1 + p_2 + p_3 + \dots$$

where P_T is the total pressure exerted by the mixture of gases when present, say in V litres; p_1, p_2, p_3, \dots are the partial pressures of the gases, respectively when present alone in the same volume, V litres.



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glucose, the mixture behaves as laevorotatory. As the reaction proceeds, the optical rotation becomes less and then it reverses *i.e.* becomes negative

Let r_0 , r_t and r_∞ be the optical rotations at time $t = 0$, $t = t$ and $t = t_\infty$ respectively, then

$$\text{Initial concentration of sucrose} = a = r_0 - r_\infty$$

$$\text{Decrease in concentration of sucrose} = x = r_0 - r_t$$

$$\text{Concentration of sucrose at any time } t = a - x$$

$$(r_0 - r_\infty) - (r_0 - r_t) = r_t - r_\infty$$

$$\text{Initial concentration of sucrose} = r_0 - r_\infty$$

$$= +24.09 - (-10.74) = +34.83$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

(i) At $t = 7.18$ sec,

$$\begin{aligned} k &= \frac{2.303}{7.18 \text{ sec}} \log \frac{34.83}{21.7 - (-10.74)} \\ &= \frac{2.303}{7.18 \text{ sec}} \log \frac{34.83}{32.44} = 11.8 \times 10^{-3} \text{ sec}^{-1} \end{aligned}$$

(ii) At $t = 18.0$ sec,

$$\begin{aligned} k &= \frac{2.303}{18 \text{ sec}} \log \frac{34.83}{17.7 - (-10.74)} \\ &= \frac{2.303}{18 \text{ sec}} \log \frac{34.83}{28.44} = 11.86 \times 10^{-3} \text{ sec}^{-1} \end{aligned}$$

(iii) At $t = 27.05$ sec,

$$\begin{aligned} k &= \frac{2.303}{27.05 \text{ sec}} \log \frac{34.83}{15 - (-10.74)} \\ &= \frac{2.303}{27.05 \text{ sec}} \log \frac{34.83}{25.74} = 11.83 \times 10^{-3} \text{ sec}^{-1} \end{aligned}$$

As the value of k is nearly constant, the reaction is of first order.

Problem 8. Hydrolysis of methyl methanoate follows first order kinetics with a rate constant of $3.60 \times 10^{-1} \text{ min}^{-1}$. What is the concentration of methyl methanoate 10 minutes after the beginning of reaction if the initial concentration of methyl methanoate was $2.50 \text{ mol litre}^{-1}$?

$$\text{Solution.} \quad \log \frac{C_2}{C_1} = -\frac{k(t_2 - t_1)}{2.303}$$

$$\log \frac{C_2 \text{ mol litre}^{-1}}{2.5 \text{ mol litre}^{-1}} = -\frac{3.60 \times 10^{-1} \text{ min}^{-1} \times (10 - 0) \text{ min}}{2.303} = -1.56$$

$$\frac{C_2}{2.5} = \text{Antilog}(-1.56) = \text{Antilog } \bar{2}.44 = 2.75 \times 10^{-2}$$

$$\text{and} \quad C_2 = 2.50 \times 2.75 \times 10^{-2} = 6.8 \times 10^{-2} \text{ mol litre}^{-1}$$

Problem 9. What percentage of the initial reactant will react in 5.0 hours of a first order reaction whose rate constant is $5.78 \times 10^{-3} \text{ sec}^{-1}$?



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Problem 15. Following data were obtained during the thermal decomposition of sulphuryl chloride at constant volume and 285°C.

| | | | | | |
|-----------------|-------------------------------------|-------------------|--------------------------|---|--------------------------|
| | $\text{SO}_2\text{Cl}_2 (\text{g})$ | \longrightarrow | $\text{SO}_2 (\text{g})$ | + | $\text{Cl}_2 (\text{g})$ |
| Time (sec) | 0 | | 240 | | 600 |
| Pressure (torr) | 180 | | 244 | | 302 |

Show that it is a first order reaction.

Solution. Let the pressure of $\text{SO}_2\text{Cl}_2 (\text{g})$ decrease by x torr. As one mole of $\text{SO}_2\text{Cl}_2 (\text{g})$ decomposes to give 1 mole of $\text{SO}_2 (\text{g})$ and 1 mole of $\text{Cl}_2 (\text{g})$ the pressure of $\text{SO}_2 (\text{g})$ increases by x torr and that of $\text{Cl}_2 (\text{g})$ also by the same value x torr.

| | | | | | |
|-------------|-------------------------------------|-------------------|--------------------------|---|--------------------------|
| | $\text{SO}_2\text{Cl}_2 (\text{g})$ | \longrightarrow | $\text{SO}_2 (\text{g})$ | + | $\text{Cl}_2 (\text{g})$ |
| Start | 180 torr | | 0 | | 0 |
| At time t | $(180 - x)$ torr | | x torr | | x torr |

$$P_T = P_{\text{SO}_2\text{Cl}_2} + P_{\text{SO}_2} + P_{\text{Cl}_2}$$

$$= 180 - x + x + x = 180 + x$$

$$x = P_T - 180 \text{ torr}$$

$$P_{\text{SO}_2\text{Cl}_2} = 180 - x$$

$$= 180 - (P_T - 180) = \boxed{360 - P_T \text{ torr}}$$

(a) At $t = 240 \text{ sec}$; $P_T = 244 \text{ torr}$

$\therefore P_{\text{SO}_2\text{Cl}_2} = 360 - 244 = 116 \text{ torr}$

$$k = \frac{2.303}{t} \log \frac{\text{Initial concentration}}{\text{Concentration at time } t}$$

$$= \frac{2.303}{240 \text{ sec}} \log \frac{180 \text{ torr}}{116 \text{ torr}}$$

$$= \frac{2.303}{240 \text{ sec}} \times 0.1909 = 0.00183 \text{ sec}^{-1}$$

At $t = 600 \text{ sec}$; $P_T = 302 \text{ torr}$

$\therefore P_{\text{SO}_2\text{Cl}_2} = 360 \text{ torr} - 302 \text{ torr} = 58 \text{ torr}$

$$k = \frac{2.303}{600 \text{ sec}} \log \frac{180 \text{ torr}}{58 \text{ torr}}$$

$$= \frac{2.303}{600 \text{ sec}} \times 0.4918 = 0.00188 \text{ sec}^{-1}$$

As the values of k are nearly constant, decomposition of sulphuryl chloride follows a first order kinetics.

Problem 16. The following data were obtained during the first order thermal decomposition of $\text{N}_2\text{O}_5 (\text{g})$ at constant volume :

| | | | | | |
|----------------------|------------------------------------|-------------------|------------------------------------|---|-------------------------|
| | $2\text{N}_2\text{O}_5 (\text{g})$ | \longrightarrow | $2\text{N}_2\text{O}_4 (\text{g})$ | + | $\text{O}_2 (\text{g})$ |
| Time (sec) | 0 | | 100 | | |
| Total pressure (atm) | 0.5 | | 0.512 | | |

Calculate the reaction rate when the total pressure is 0.52 atm.

Solution. Let the pressure of $\text{N}_2\text{O}_5 (\text{g})$ decrease by $2x$ atm. As 2 moles of N_2O_5



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Since 1 mol of ethyl acetate hydrolyses to produce 1 mol of acetic acid.

Amount of acetic acid at time $t \propto$ Amount of ethyl acetate that hydrolyses

(iii) At time $t = \infty$, the solution contains HCl and acetic acid (Ethyl acetate is not present as it has hydrolysed completely). Let volume of alkali used to neutralize this solution be V_{∞} .

Volume of alkali that neutralizes acetic acid at time $t_{\infty} = V_{\infty} - V_0$

As the acetic acid present $= \infty$ has resulted from the
in the solution at time t complete hydrolysis of ethyl acetate

\therefore Volume of alkali used for neutralizing acetic acid at t_{∞} = Initial amount of ethyl acetate present at $t = 0$
= $V_{\infty} - V_0$

Also, Amount of acetic acid present = Amount of ethyl acetate that hydrolyses
= $V_t - V_0$

\therefore Amount of ethyl acetate that remains unreacted at time t = Initial amount of ethyl acetate - Amount of reacted ethyl acetate
= $(V_{\infty} - V_0) - (V_t - V_0) = V_{\infty} - V_t$

Using first order rate equation :

$$k = \frac{2.303}{t} \log \frac{\text{Initial concentration of ethyl acetate}}{\text{Concentration of ethyl acetate at time } t}$$

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

(i) When $t = 10$ min,

$$k = \frac{2.303}{10 \text{ min}} \log \frac{25 - 10}{25 - 10.62} = \frac{2.303}{10 \text{ min}} \log \frac{15}{14.38} = 0.0042 \text{ min}^{-1}$$

(ii) When $t = 20$ min,

$$k = \frac{2.303}{20 \text{ min}} \log \frac{25 - 10}{25 - 11.21} = \frac{2.303}{20 \text{ min}} \log \frac{15}{13.79} = 0.00416 \text{ min}^{-1}$$

(iii) When $t = 100$ min,

$$k = \frac{2.303}{100 \text{ min}} \log \frac{25 - 10}{25 - 15.20} = \frac{2.303}{100 \text{ min}} \log \frac{15}{9.80} = 0.00425 \text{ min}^{-1}$$

(iv) When $t = 150$ min,

$$k = \frac{2.303}{150 \text{ min}} \log \frac{25 - 10}{25 - 17.11} = \frac{2.303}{150 \text{ min}} \log \frac{15}{7.89} = 0.00425 \text{ min}^{-1}$$

As the value of k is nearly constant, hydrolysis of ethyl acetate in presence of excess of acid is a first order reaction.

Problem 22. The catalytic decomposition of N_2O by gold at 900°C and at an initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

(a) What is the order of the reaction ?

(b) How much of it will decompose in 100 min at the same temperature but at initial pressure of 600 mm ?
(Roorkee 1990)



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$$2.0 \times 10^{-4} = \frac{2.303}{200 \text{ min}} \log \frac{100}{100-x}$$

$$\log \frac{100}{100-x} = \frac{2.0 \times 10^{-4} \times 200}{2.303} = 0.01737$$

$$\frac{100}{100-x} = \text{Antilog } 0.1737 \times 10^{-1} = 1.1491$$

$$100-x = \frac{100}{1.1491} = 87$$

$$x = 100 - 87 = 13$$

$$\text{Amount of reactant converted in 200 min} = \frac{13}{100} \times 0.2 \text{ mol dm}^{-3} = 0.026 \text{ mol dm}^{-3}.$$

Problem 27. The half time of first order decomposition of nitramide is 2.1 hour at 15°C.



If 6.2 g of NH_2NO_2 is allowed to decompose, calculate (i) time taken for NH_2NO_2 to decompose 99% ; and (ii) volume of dry N_2O produced at this point, measured at STP. (Roorkee 1994)

Solution.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1 \text{ hour}} = 0.33 \text{ hr}^{-1}$$

$$t = \frac{2.303}{k} \log \left[\frac{\text{Initial concentration}}{\text{Concentration at time } t} \right]$$

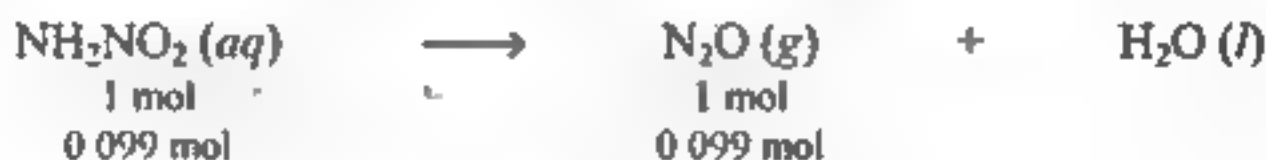
$$= \frac{2.303}{0.33 \text{ hr}^{-1}} \times \log \frac{100}{100-99}$$

$$= \frac{2.303}{0.33} \times \log 10^2 = \frac{2.303}{0.33} \times 2 = 13.96 \text{ hr}$$

$$\text{Molecular mass of } \text{NH}_2\text{NO}_2 = 14 + 2 \times 1 + 14 + 2 \times 16 = 62 \text{ amu}$$

$$\text{Moles of } \text{NH}_2\text{NO}_2 \text{ taken} = \frac{6.2 \text{ g}}{62 \text{ g/mol}} = 0.1 \text{ mol}$$

$$\text{Moles of } \text{NH}_2\text{NO}_2 \text{ decomposed} = \frac{99}{100} \times 0.1 \text{ mol} = 0.099 \text{ mol}$$



As 1 mol of NH_2NO_2 decomposes to give 1 mole of N_2O

$$\therefore \text{Moles of } \text{N}_2\text{O} \text{ formed} = 0.099 \text{ mol}$$

$$1 \text{ mol of a gas} = 22.4 \text{ litres at STP}$$

$$0.099 \text{ mol } \text{N}_2\text{O} = \frac{0.099 \text{ mol}}{1 \text{ mol}} \times 22.4 \text{ L} = 2.217 \text{ L}$$

$$\text{Volume of dry } \text{N}_2\text{O} \text{ produced at STP} = 2.217 \text{ L}$$



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PROBLEMS FOR PRACTICE

1. Hydrogen combines with iodine to form hydrogen iodide. The initial concentration of iodine was 0.5432 moles per litre and the concentration after 45 minutes was 0.3484 moles per litre. What is the average rate of the reaction?
2. For a chemical reaction $A \longrightarrow B$, for every 0.2 mol dm^{-3} of B formed, what happens to the concentration of A?
3. In a first order reaction the initial concentration of the reactant was $0.05 \text{ mol litre}^{-1}$ and the rate constant is $1.5 \times 10^{-3} \text{ sec}^{-1}$. What was the initial rate of the reaction?
4. The rate constant for the first order decomposition of dibromosuccinic acid at 60°C is $6.54 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$. What is the rate of reaction when the concentration of dibromosuccinic acid is $3.0 \text{ mol litre}^{-1}$?

5. Following results were obtained in the decomposition of nitrogen pentoxide on standing to produce dinitrogen tetroxide and oxygen. Show by calculation that the decomposition is of first order.

| | | | | | |
|--------------------------------------|------|------|------|------|------|
| $t \text{ (sec):}$ | 0 | 184 | 319 | 526 | 1198 |
| $C \text{ (mol litre}^{-1}\text{):}$ | 2.33 | 2.08 | 1.91 | 1.67 | 1.11 |

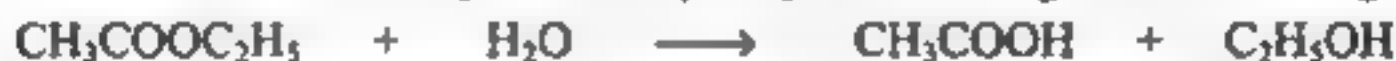
where C is the concentration of dinitrogen pentoxide

6. The polarimeter reading in an experiment to measure the rate of inversion of cane-sugar were as follows:

| | | | | | |
|-----------|-------|-------|-------|-------|----------|
| Time/min: | 0 | 10 | 20 | 30 | ∞ |
| Rotation: | +32.4 | +28.8 | +25.5 | +22.4 | -14.0 |

What is the order of the reaction? Calculate the rate constant also.

7. 10 mL of ethyl acetate was added to a flask containing V mL of 0.1 N HCl placed in a thermostat at 60°C . Ethyl acetate hydrolysis according to the following equation:



10 ml of the reaction mixture was withdrawn at different intervals of time, chilled to stop the hydrolysis and then titrated against a standard alkali. The following data were obtained:

| | | | | | | |
|--------------------|----|-------|-------|-------|-------|----------|
| Time (minutes): | 0 | 10 | 20 | 100 | 150 | ∞ |
| ml of alkali used: | 10 | 10.62 | 11.21 | 15.20 | 17.11 | 25 |

Show that the hydrolysis of ethyl acetate is a first order reaction.

8. A first order reaction has a specific reaction rate of $1.0 \times 10^{-3} \text{ sec}^{-1}$. How much time will it take for 10 g of the reactant to reduce to half the quantity?
9. Calculate the value of $[\text{N}_2\text{O}_5]$ 50 minutes after the beginning of the reaction if its initial concentration is $0.1 \text{ mol litre}^{-1}$ and rate constant is $2.33 \times 10^{-2} \text{ min}^{-1}$.
10. Find the two-third life, $t_{2/3}$ of a first order reaction in which $k = 5.48 \times 10^{-14} \text{ sec}^{-1}$.
11. A first order reaction is found to have a rate constant $k = 7.39 \times 10^{-5} \text{ sec}^{-1}$. Calculate $t_{1/3}$ of the reaction.
12. The rate constant of a first order reaction is $7.39 \times 10^{-5} \text{ sec}^{-1}$ at 150°C . How long will it take for the reaction to be 75% completed?
13. The reaction $A \longrightarrow B$ is first order. If it takes 15 seconds for 20% of the original material to react, calculate the specific rate constant.
14. The rate of inversion of cane-sugar is of the first order. If 25% of a sample of cane-sugar is hydrolysed in 50 seconds, how long will it take for 50% to be hydrolysed?



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4. **Temperature-coefficient.** It is defined as the ratio of the specific rate constants at two temperatures separated by 10°C .

$$\text{Temperature coefficient} = \frac{k_2 \text{ at } (t + 10)^\circ\text{C}}{k_1 \text{ at } t^\circ\text{C}}$$

For most of the reactions, an increase in temperature of 10°C doubles or triples the rate of reaction.

5. A graph of $\log k$ versus $1/T$ gives a straight line whose slope is $-E_a/2.303 R$ from which activation energy, E_a , can be calculated. The intercept is $\log A$ where A is the frequency factor.

6. **Collision frequency (z) and steric factor (p)**

$$\text{Frequency factor, } A = pz$$

The collision frequency, z , is the number of collisions between reactant molecules per second, when the concentration of each reactant is 1 mol litre^{-1} . It is found by calculations to have nearly the same value but as reactions have different reaction rates this is multiplied by the steric factor, p . The steric factor, in fact, gives the percentage of collisions with the proper orientation needed for the reaction.

✓ SOLVED PROBLEMS

Problem 1. The activation energy for the decomposition of hydrogen iodide at 581 K is $209.5 \text{ kJ mol}^{-1}$. Calculate the fraction of molecules having energy equal to activation energy.

$$\begin{aligned} \text{Solution. Fraction of molecules with energy equal to activation energy} &= e^{-E_a/RT} \\ &= \frac{-209.5 \times 10^3 \text{ J}}{8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times 581 \text{ K}} = e = 2.11 \times 10^{-19} \end{aligned}$$

Problem 2. Calculate the rate constant at 400 K for the following reaction :



Arrhenious factor is $4.3 \times 10^{10} \text{ sec}^{-1}$ and activation energy is $103344 \text{ J mol}^{-1}$.

$$\begin{aligned} \text{Solution. } \log k &= \log A - \frac{E_a}{2.303 RT} \\ &= \log 4.3 \times 10^{10} \text{ sec}^{-1} - \frac{103344 \text{ J mol}^{-1}}{2.303 \times 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}} \\ &= 10.6335 - 13.5900 = \bar{3}.1435 \\ k &= \text{Antilog } \bar{3}.1435 = 0.001392 \text{ sec}^{-1} \end{aligned}$$

Problem 3. The decomposition of phosphine



has the rate law : $\text{Rate} = k [\text{PH}_3]$

The rate constant is $6.0 \times 10^{-4} \text{ sec}^{-1}$ at 27°C and activation energy is $3.05 \times 10^5 \text{ J mol}^{-1}$. What is the value of rate constant at 37°C ?

$$\begin{aligned} \text{Solution. } T_1 &= 27^\circ\text{C} + 273 = 300 \text{ K}; \\ T_2 &= 37^\circ\text{C} + 273 = 310 \text{ K} \end{aligned}$$



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$$k_2 \text{ at } 47^\circ\text{C} = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \text{ min}} = 0.0693 \text{ min}^{-1}$$

$$E_a = 2.303 R \left[\frac{T_1 T_2}{T_2 - T_1} \right] \left[\log \frac{k_2}{k_1} \right]$$

$$T_1 = 273 + 27^\circ\text{C} = 300 \text{ K}$$

$$T_2 = 273 + 47^\circ\text{C} = 320 \text{ K}$$

$$\left[\frac{T_1 T_2}{T_2 - T_1} \right] = \frac{(300 \text{ K})(320 \text{ K})}{(320 - 300 \text{ K})} = 4800 \text{ K}$$

$$\log \frac{k_2}{k_1} = \log \frac{0.0693 \text{ min}^{-1}}{0.0231 \text{ min}^{-1}} = \log 3 = 0.4771$$

$$E_a = (2.303)(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(4800 \text{ K})(0.4771) \\ = 43848 \text{ J/mol} = 43.848 \text{ kJ/mol}$$

Problem 12. In the Arrhenius equation for a reaction the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be ten minutes? (IIT/JEE 1990)

Solution. $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \text{ min}} = \frac{0.693}{10 \times 60 \text{ sec}} = 0.0012 \text{ sec}^{-1}$

$$\log k = \log 0.0012 \text{ sec}^{-1} = -2.9208$$

$$\log A = \log 4 \times 10^{13} \text{ sec}^{-1} = 13.6021$$

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

$$\frac{E_a}{2.303 RT} = \log A - \log k$$

$$T = \frac{E_a}{2.303 R (\log A - \log k)} \\ = \frac{98.6 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} (13.6021) - (-2.9208)} \\ = \frac{98.6 \times 10^3}{2.303 \times 8.314 \times 16.5229} = 311.7 \text{ K.}$$

Problem 13. Two reactions (i) $A \longrightarrow \text{products}$; (ii) $B \longrightarrow \text{products}$, follows first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K. (IIT/JEE 1992)



$$k_A(310) = \frac{0.693}{30 \text{ min}} = 0.0231 \quad (1)$$



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Comparing this equation with Arrhenius equation

$$\log k = \frac{-E_a}{2.303 R} \times \frac{1}{T} + \log A, \text{ one has}$$

$$\frac{-E_a}{2.303 R} = -1.25 \times 10^4$$

$$\therefore E_a = 1.25 \times 10^4 \times 2.303 \times 8.314 = 239.94 \text{ kJ mol}^{-1}$$

(ii) For first order reaction

$$t_{0.5} = 0.693/k,$$

$$k = \frac{0.693}{256 \times 60} \text{ s}^{-1}$$

$$\therefore \log \frac{0.693}{256 \times 60} = 14.34 - \frac{1.25 \times 10^4}{T} k$$

$$-4.35 = 14.34 - \frac{1.25 \times 10^4}{T}, \text{ or } \frac{1.25 \times 10^4}{T} = 18.69$$

$$\therefore T = \frac{1.25 \times 10^4}{18.69} = 668.80 \text{ K}$$

Problem 18. The rate constant of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ s}^{-1}$ at 100°C . Evaluate the Arrhenius parameters A and E_a . (IIT/JEE 1998)

Solution.

$$k_1 = 1.5 \times 10^7 \text{ s}^{-1}$$

$$T_1 = 50^\circ = 273 + 50 = 323 \text{ K}$$

$$T_2 = 100^\circ\text{C} = (273 + 100) \text{ K} = 373 \text{ K}$$

$$k_2 = 4.5 \times 10^7$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots(i)$$

$$E_a = \log \frac{k_2}{k_1} \times 2.303 R \times \frac{T_1 T_2}{T_2 - T_1}$$

$$= \log \frac{4.5 \times 10^7}{1.5 \times 10^7} \times 2.303 \times 8.314 \times \left(\frac{373 \times 323}{373 - 323} \right)$$

$$= 0.6990 \times 2.303 \times 8.314 \times \frac{373 \times 323}{50} = 22.012 \text{ kJ}$$

Putting the value of E_a into eqn. (i), we get

$$\log A = \log k + \frac{E_a}{2.303 RT}$$

$$= \log 1.5 \times 10^7 + \frac{22.012 \times 10^3 \text{ J}}{2.303 \times 8.314 \times 323}$$

$$= -7.176 + 3.6 = 10.776$$

$$A = \text{Antilog } 10.776$$

$$= 5.97 \times 10^{10} \text{ s}^{-1}$$



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Chemical Equilibrium-I

- 1. Reversible reaction.** It does not go to completion because some of the products formed react to give back the reactants.
- 2. Chemical equilibrium.**
 - (a) When a reaction or system attains chemical equilibrium, the speed at which reactants combine to give products is equal to the speed at which the products combine to give back the reactants.
 - (b) The chemical equilibrium is said to be *dynamic* in nature because reactant molecules are combining continuously to give products and the product molecules are combining at the same rate to give back the reactants, *i.e.*, the chemical activity does not cease.
 - (c) At equilibrium no further net chemical change occurs and, therefore, the composition (Molar concentrations) of the reactants and products remain constant. These are called *equilibrium concentrations*.
 - (d) At equilibrium, rate of forward-reaction (combination of reactants) is equal to the rate backward-reaction (combination of products).

$$R_f = R_b$$

- (e) The equilibrium position of a reversible-reaction can be changed by changing the concentration of a reactant or product or volume of the reaction vessel, pressure and temperature (*Le-Chatelier principle*).
- 3. The law of mass action.** The rate of a chemical-reaction is directly proportional to the concentration of a reacting substances raised to a power given by the coefficient in the balanced chemical-equation.

For a reversible-reaction :



the rate at which A and B react at equilibrium is proportional to the equilibrium concentrations of A and B raised to a power given by the coefficients in the balanced chemical equation.

$$\therefore \text{Rate}_{(\text{forward})} R_f \propto [A]^a [B]^b = k_1 [A]^a [B]^b$$

where k_1 is a proportionality constant called rate constant or velocity constant for the forward reaction.

Similarly, the rate at which the products G and H react at equilibrium to give back the reactants is directly proportional to the equilibrium concentrations of G and H raised to a power given by their coefficients in the balanced chemical equation.

$$\therefore \text{Rate}_{(\text{Backward})} R_b \propto [G]^g [H]^h = k_2 [G]^g [H]^h$$

where k_2 is the rate constant or velocity constant for the backward reaction. At equilibrium, the rate of forward reaction is equal to the rate of backward reaction.



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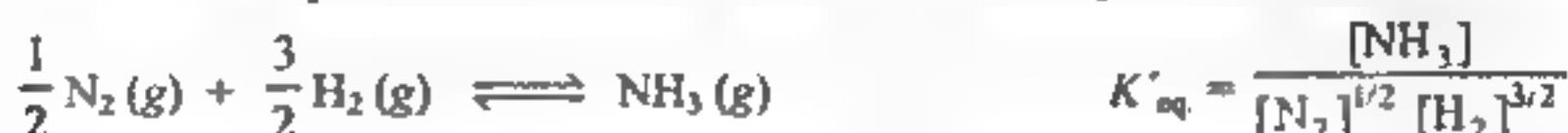


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(ii) The value of equilibrium constant is 3.86×10^{-3} if the equation is written as



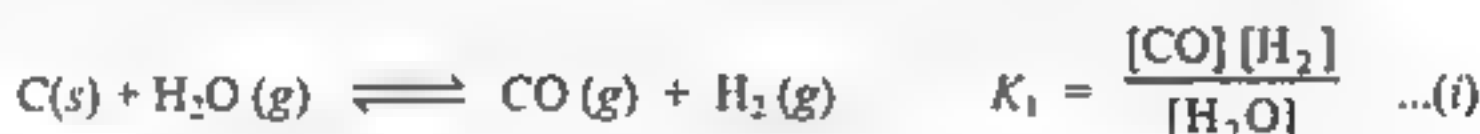
11. The value of the equilibrium constant changes with change in temperature. For the reaction :



the value of equilibrium constant is 45.9 at 490°C and 64 at 445°C .

12. The value of the equilibrium constant of a reaction does not change in presence of a catalyst.

13. Equilibrium constants for chemical equations can be combined to obtain equilibrium constants for other equations. Consider the following reactions:



For the reaction,



Multiplying eqn. (i) and eqn. (ii), one has

$$\begin{aligned} K_3 &= K_1 \times K_2 \\ &= \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]} \times \frac{[\text{H}_2\text{O}]^2}{[\text{CO}_2][\text{H}_2]^2} = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} \end{aligned}$$

14. (i) Write the balanced chemical equation for the reversible reaction and formulate the equilibrium-constant expression.



$$K_c = \frac{[\text{H}_2][\text{A}]^2}{[\text{HA}]^2}$$

$$K_p = \frac{p_{\text{H}_2} \times p_{\text{A}}^2}{p_{\text{HA}}^2}$$

(ii) Use equilibrium concentrations (or partial pressures) for the reactants and products.

(iii) If equilibrium concentrations (or partial pressures) are not given, first calculate their values from the data given in the problem.

15. (i)

$$\begin{aligned} pV &= nRT \\ p &= \frac{n}{V} RT \\ p &= CRT \end{aligned}$$

where, C is concentration in mol/litre.

or partial pressure \propto Concentration

\propto Number of moles

\propto Number of molecules.



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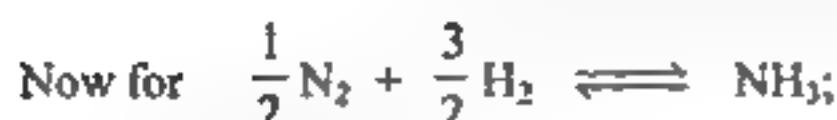
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$$K_c = \frac{4 \times (0.0025)^2 \times 4^2}{(1 - 0.0025)(3 - 3 \times 0.0025)^3}$$

$$K_c = 1.49 \times 10^{-5} \text{ litre}^2 \text{ mol}^{-2}$$



$$K_{c_1} = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}}$$

$$\therefore K_{c_1} = \sqrt{(K_c)} = 3.86 \times 10^{-3} \text{ litre mol}^{-1}$$

Problem 19. A mixture of SO_2 , SO_3 and O_2 gases is maintained in a 100 litre flask at a temperature at which the equilibrium constant (K_c) for the reaction :



is 100.

(Roorkee 1987)

- (i) If the number of moles of SO_2 and SO_3 in the flask are equal, how many moles of O_2 are present ?
- (ii) If the number of moles of SO_3 in the flask is twice the number of moles of SO_2 how many moles of O_2 are present ?

Solution. (a) For the reaction :



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

- (i) Let number of moles of SO_2 be n moles.

$$\begin{aligned} \text{Number of moles of SO}_3 &= \text{Number of moles of SO}_2 \\ &= n \text{ moles} \end{aligned}$$

$$[\text{O}_2] = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \times K_c}$$

$$\left(\frac{x \text{ mol}}{10 \text{ L}} \right) = \frac{(n \text{ mol} / 10 \text{ L})^2}{(n \text{ mol} / 10 \text{ L})^2 \times 100}$$

$$x = \frac{10}{100} = 0.1 \text{ mol}$$

- (ii) Moles of $\text{SO}_2 = n$

$$\text{Moles of SO}_3 = 2n$$

$$[\text{O}_2] = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \times K_c}$$

$$\frac{x \text{ mol}}{10 \text{ L}} = \frac{(2n \text{ mol} / 10 \text{ L})^2}{(n \text{ mol} / 10 \text{ L})^2 \times 100}$$

$$x = \frac{4n^2 \times 10}{n^2 \times 100} = 0.4 \text{ mol}$$



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$$\alpha^2 = \frac{0.2667}{0.6667} = 0.4$$

$$\alpha = 0.63$$

$$\text{Percent Dissociation} = 0.63 \times 100 = 63\%$$

Problem 24. For the reaction $\text{CO (g)} + 2\text{H}_2 \text{ (g)} \rightleftharpoons \text{CH}_3\text{OH (g)}$, hydrogen gas is introduced into a five-litre flask at 327°C , containing 0.2 mole of CO (g) and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of $\text{CH}_3\text{OH (g)}$ is formed. Calculate the equilibrium constants, K_p and K_c . (IIT/JEE 1990)

Solution. $PV = nRT$

$$\begin{aligned} \text{Total number of moles at equilibrium} &= \frac{PV}{RT} \\ &= \frac{4.92 \text{ atm} \times 5\text{L}}{0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times (327 + 273 \text{ K})} = 0.5 \text{ mol} \end{aligned}$$



$$\text{Total number of moles} = \text{Moles CO} + \text{moles H}_2 + \text{moles CH}_3\text{OH}$$

$$0.5 \text{ mol} = 0.1 \text{ mol} + \text{moles H}_2 + 0.1 \text{ mol}$$

$$\text{moles H}_2 = 0.5 - 0.1 - 0.1 = 0.3 \text{ mol}$$

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2} = \frac{(0.1/5)}{(0.1/5) (0.3/5)^2}$$

$$= \frac{0.1}{5} \times \frac{5}{0.1} \left(\frac{5}{0.3} \right)^2 = 277.8$$

$$\begin{aligned} \Delta n &= \text{Number of molecules of the gaseous products} \\ &\quad - \text{Number of molecules of the gaseous reactants} \\ &= 1 - (1 + 2) = -2 \end{aligned}$$

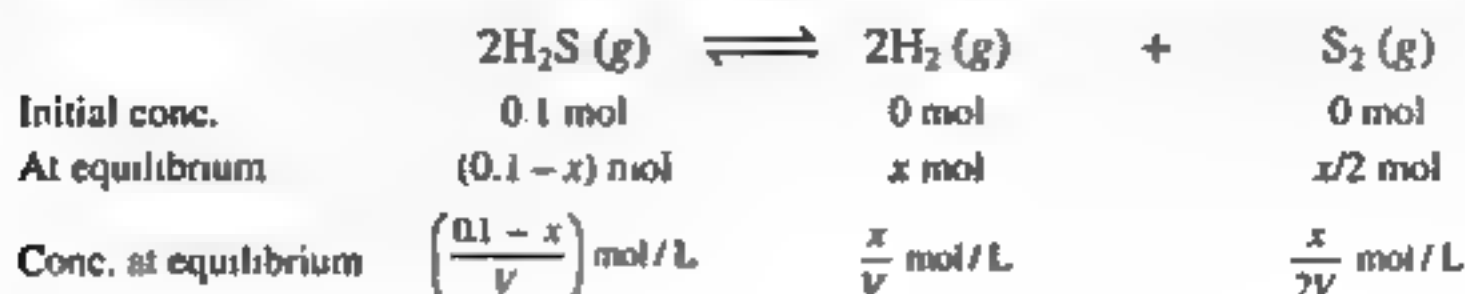
$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} \\ &= 277.8 \times (0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 600 \text{ K})^{-2} \\ &= \frac{277.8}{(0.082 \times 600)^2} = 0.1147 \end{aligned}$$

Problem 25. Calculate the percent dissociation of $\text{H}_2\text{S (g)}$ if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1,000 K. For the reaction,



the value of K_c is 1.0×10^{-6} . (Roorkee 1994)

Solution. Let x mol of H_2S dissociate to give x mole of H_2 and $x/2$ mol of S_2 .





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If the concentration of PCl_5 is doubled by injecting 1.75 mol PCl_5 into the reaction mixture, what will be the concentration of PCl_5 when the new equilibrium is reached at 150°C ?

9. At 1100 K, K_p for the reaction :



its 7.7×10^{-6} .

(a) What is K_c of the reaction ?

(b) What is K_c at 10 atmosphere and 1100 K ?

10. The equilibrium constant of the reaction :



is 4 at 298 K. What is the weight of methyl acetate in equilibrium mixture if 2 moles of methyl alcohol were originally mixed with one mole of acetic acid ?

11. When 60 g of ethanoic acid were heated with 46 g ethanol until equilibrium was reached, 66.5% alcohol gets converted into an ester. How much ester will be formed if 4 moles of acetic acid and one mole of alcohol were heated together ?

ANSWERS

1. 2.5×10^{-3}

2. $[\text{A}] = 0.334 \text{ mol/litre}$

3. 0.00069

$[\text{B}] = 1.334 \text{ mol/litre}$

$[\text{AB}] = 3.332 \text{ mol/litre}$

4. (a) 0.0665 mol/litre

5. $K_c = 1.58$

6. $4 \times 10^{-3} \text{ mol/litre}$

(b) 3.94

$[\text{CO}_2] = 0.15 \text{ mol/litre}$

$K_p = 2.39 \text{ atm}^{-1}$

$[\text{CO}_2] = 0.05 \text{ mol/litre}$

7. (a) 64.5

8. 3.4 mol/litre

9. $K_c = 8.53 \times 10^{-3}$

(b) 0.0155

$K_x = 7.7 \times 10^{-7}$

10. 62.53 g/litre

11. 81.84 g/litre



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$$\begin{aligned}
 p_{\text{CO}_2} &= \frac{\text{Number of moles of CO}_2}{\text{Total number of moles}} \times \text{Total pressure} \\
 &= \frac{1}{3} \times 0.225 = 0.075 \text{ atm} \\
 K_p &= p_{\text{CO}_2} \times (p_{\text{NH}_3})^2 \\
 &= 0.075 \times (0.15)^2 = 1.69 \times 10^{-2}
 \end{aligned}$$

(ii) Addition of an inert gas does not change K_p because the partial pressures of NH_3 and CO_2 are unaffected. But the total pressure of the mixture of gases increases by the introduction of an inert gas in the same volume.

Problem 7. One mole of N_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated to 227°C . The equilibrium pressure is 2.05 atmospheres. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction.



Solution. N_2 does not react with any of the gases present in the vessel and therefore its partial pressure corresponding to one mole of the gas remains the same.

Let α be the degree of dissociation of PCl_5 .

| | $\text{N}_2(\text{g})$ | + | $\text{PCl}_5(\text{g})$ | \rightleftharpoons | $\text{PCl}_3(\text{g})$ | + | $\text{Cl}_2(\text{g})$ |
|---------|------------------------|---|-------------------------------|----------------------|--------------------------|---|-------------------------|
| Initial | 1 mole | | 3 moles | | 0 | | 0 |
| Final | 1 mole | | $3(1 - \alpha) = 3 - 3\alpha$ | | 3α | | 3α |

Total number of moles in the 100 litre vessel = $1 + 3 - 3\alpha + 3\alpha + 3\alpha = 4 + 3\alpha$

$$p_{\text{PCl}_5} = \text{Mole fraction} \times \text{Total pressure}$$

$$= \frac{3 - 3\alpha}{4 + 3\alpha} \times 2.05 \text{ atm}$$

$$p_{\text{PCl}_3} = \frac{3\alpha}{4 + 3\alpha} \times 2.05 \text{ atm}$$

$$p_{\text{Cl}_2} = \frac{3\alpha}{4 + 3\alpha} \times 2.05 \text{ atm}$$

$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}}$$

$$= \frac{\frac{3\alpha}{4 + 3\alpha} \times 2.05 \times \frac{3\alpha}{4 + 3\alpha} \times 2.05}{\frac{3 - 3\alpha}{4 + 3\alpha} \times 2.05}$$

$$= \frac{9\alpha^2 \times 2.05}{(4 + 3\alpha)(3 - 3\alpha)}$$

$$K_c = \frac{\frac{3\alpha}{100} \times \frac{3\alpha}{100}}{\frac{3 - 3\alpha}{100}} = \frac{9\alpha^2}{100} \times \frac{1}{3 - 3\alpha}$$

$$K_p = K_c (RT)^{\Delta n} \quad \Delta n = 2 - 1 = +1$$



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Problem 11. Ammonia under a pressure of 15 atmospheres at 27°C is heated to 347°C in a closed vessel in the presence of a catalyst. Under these conditions, NH_3 is partially decomposed according to the equation, (JIT/JEE 1970)



The vessel is such that the volume remains effectively constant whereas pressure increases to 50 atmospheres. Calculate the percentage of ammonia decomposed.

Solution. Let α be the degree of dissociation of ammonia under these conditions. According to the balanced equation α moles of NH_3 decompose to produce $\alpha/2$ mole of N_2 and $3/2 \alpha$ moles of H_2 .



If the number of mole in the beginning is 1, then at equilibrium

$$1 - \alpha \qquad \alpha/2 \qquad 3/2 \alpha$$

$$\text{Total number of moles after decomposition} = 1 - \alpha + \alpha/2 + 3/2 \alpha = 1 + \alpha$$

Using Gay Lussac's law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\begin{aligned} P_2 &= P_1 \times \frac{T_2}{T_1} = 15 \times \frac{273 + 347}{273 + 27} \\ &= 15 \times \frac{620}{300} = 31 \text{ atm} \end{aligned}$$

$$\frac{\text{Number of moles without decomposition at temperature } T}{\text{Number of moles after decomposition at the same temperature } T} = \frac{P_a}{P_b}$$

$$\frac{1}{1 + \alpha} = \frac{31 \text{ atm}}{50 \text{ atm}} = 0.613$$

$$\% \text{ decomposition of } \text{NH}_3 = 0.613 \times 100 = 61.3\%$$

Problem 12. At a certain temperature the vapour density of N_2O_4 is 30.2. Calculate its percentage dissociation at this temperature.

Solution. Let α be the degree of dissociation of N_2O_4



Initial Conc

1

0

Conc. at equilibrium

$1 - \alpha$

2α

$$\text{Total number of moles after dissociation} = 1 - \alpha + 2\alpha = 1 + \alpha$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \quad (\text{Total mass in a closed vessel is constant})$$

$$\propto \frac{1}{\text{Volume}}$$

Let 1 mole of gases occupy a volume of V litres at some pressure P .

$\therefore (1 + \alpha)$ moles of gases will occupy a volume of $V(1 + \alpha)$ litres at the same pressure P .

$$\text{Density } (D) \text{ of undissociated } \text{N}_2\text{O}_4 \propto \frac{1}{V}$$

$$\text{Density } (d) \text{ after dissociation} \propto \frac{1}{V(1 + \alpha)}$$



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$$= -\frac{2.52 \pm 3.02}{0.74} = 0.676$$

(i) Number of moles of H_2 present at equilibrium = 0.676 mol

$$(ii) \quad p_{\text{CO}} = \frac{3 - 0.676}{2} = 1.162 \text{ atm}$$

$$p_{\text{H}_2\text{O}} = \frac{1 - 0.676}{2} = 0.162 \text{ atm}$$

$$p_{\text{CO}_2} = \frac{0.676}{2} = 0.338 \text{ atm}$$

$$p_{\text{H}_2} = \frac{0.676}{2} = 0.338 \text{ atm}$$

Problem 19. At room temperature the following reactions proceed nearly to completion :



The dimer, N_2O_4 , solidifies at 262 K. A 250 mL flask and a 100 mL flask are separated by a stopcock. At 300 K the nitric oxide in the larger flask exerts a pressure of 1.053 atm and the smaller one contains oxygen at 0.789 atm. The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled to 220 K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to behave ideally.) (IIT/JEE 1992)

Solution. $PV = nRT$ or $n = \frac{PV}{RT}$

$$\begin{aligned} \text{Moles of NO in the larger flask} &= \frac{1.053 \text{ atm} \times (250/1000) \text{ L}}{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} \\ &= 0.0107 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Moles of O}_2 \text{ in the smaller flask} &= \frac{0.789 \text{ atm} \times (100/1000) \text{ L}}{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} \\ &= 0.0032 \text{ mol} \end{aligned}$$



$$\text{Moles of NO that react with } 0.0032 \text{ mol O}_2 = 2 \times 0.0032 \text{ mol} = 0.0064 \text{ mol}$$

$$\begin{aligned} \text{Moles of NO left unreacted} &= 0.0107 \text{ mol} - 0.0064 \text{ mol} \\ &= 0.0043 \text{ mol} \end{aligned}$$

At 200 K, there is no N_2O_4 (or NO_2) as it solidifies at 262 K and so the flask contains unreacted NO in $250 + 100 = 350 \text{ mL}$ Volume.

$$\begin{aligned} \text{Pressure of NO gas left} &= \frac{nRT}{V} \\ &= \frac{0.0043 \text{ mol} \times 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 220 \text{ K}}{(350/1000) \text{ L}} \\ &= 0.221 \text{ atm} \end{aligned}$$



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$$x = \text{moles of O}_2 \text{ reacted}$$

If the yield is 80%, then

$$2x = 2a \times \frac{80}{100} = 1.6a$$

or $x = 0.8a$

$$\text{Moles of H}_2 \text{ left after the reaction} = 2a - (0.8 \times 2) = 0.4a$$

$$\text{Moles of O}_2 \text{ left after the reaction} = \frac{0.4a}{2} = 0.2a$$

$$\text{Moles of H}_2\text{O formed} = 2 \times 0.8a = 1.6a$$

$$\text{Total moles of H}_2, \text{O}_2, \text{H}_2\text{O in the gaseous phase} = 0.4a + 0.2a + 1.6a = 2.2a$$

Given $P = 0.8 \text{ atm}, T = 20^\circ\text{C} + 273 = 293 \text{ K}$

$$\text{Initial moles} = 2a + a + 0 = 3a$$

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{3a \times R \times 293}{0.8} \quad \dots(i)$$

After the reaction, $n = 2.2a$ and volume remains constant

$$T = 120^\circ\text{C} + 273 = 393 \text{ K}$$

$$V = \frac{2.2a \times R \times 393}{P} \quad \dots(ii)$$

Comparing relation (i) & (ii), one has

$$\therefore V = \frac{2.2a \times R \times 393}{P} = \frac{3a \times R \times 293}{0.8}$$

or $P = \frac{393 \times 0.8 \times 2.2}{3 \times 293} = 0.787 \text{ atm}$

Problem 30. At 837°C , K_p for the reaction between $\text{CO}_2(\text{g})$ and excess hot graphite (s) is 10 atm.

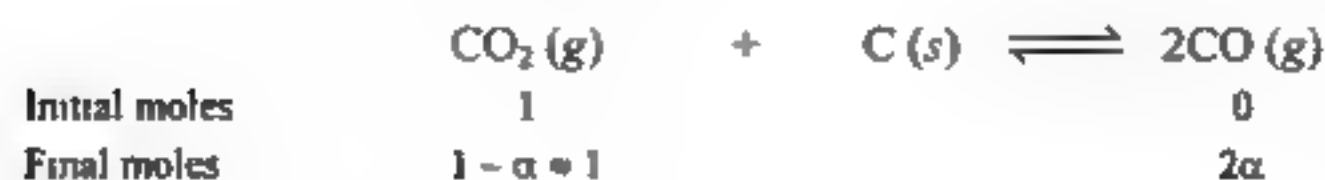
(a) What are the equilibrium concentration of the gases at 837°C and a total pressure of 5 atm?

(b) At what total pressure, the gas contains 5% CO_2 by volume? (IIT/JEE 2000)



$$\Delta n = \text{Moles of gaseous products} - \text{Moles of gaseous reactants} \\ = 2 - 1 = 1$$

$$K_p = K_c (RT)^{\Delta n} = K_c \times RT \quad \text{or} \quad K_c = \frac{K_p}{RT} = 0.1098$$





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Effect of Temperature on Equilibrium Constant

1. A change of temperature affects the rates of both forward and backward reactions of a reversible-reaction but not necessarily to the same extent.
2. A change of temperature changes the value of an equilibrium constant.
3. The rise in temperature increases the value of equilibrium constant of an endothermic reversible-reaction but decreases the value of equilibrium constant of an exothermic reaction.
4. The effect of temperature on an equilibrium constant is described by the following equations :

$$(i) \quad \frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad \text{where, } R \text{ is } 8.31 \text{ J/K-mol}$$

where ΔH° is the molar enthalpy change for the reaction and is assumed that it does not change with temperature.

$$(ii) \quad K = -\frac{\Delta H^\circ}{RT} + C$$

$$(iii) \quad \log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

✓ SOLVED PROBLEMS

Problem 1. For the equilibrium



ΔH° is -196.6 kJ/mol . What is the equilibrium constant for the reaction at 1000°C ? The equilibrium constant at 800 K is 1.12×10^3 .

Solution.

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\begin{aligned} \log \frac{K_2}{K_1} &= -\frac{196.6 \times 10^3 \text{ J/mol}}{2.303 \times 8.31 \text{ J K mol}} \left(\frac{1}{800} - \frac{1}{1273} \right) \\ &= -4.77 \end{aligned}$$

$$\begin{aligned} \frac{K_2}{K_1} &= \text{Antilog } -4.77 = \text{Antilog } -5.23 \\ &= 1.698 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} K_2 &= 1.698 \times 10^{-5} \times K_1 \\ &= 1.698 \times 10^{-5} \times 1.12 \times 10^3 \\ &= 1.9 \times 10^{-3} \end{aligned}$$



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If the degree of dissociation (α) of a weak-electrolyte is very small compared to 1, $(1 - \alpha)$ is approximately equal to 1 so that equation (i) now becomes :

$$K = C\alpha^2$$

or

$$\alpha = \sqrt{\frac{K}{C}} \quad \dots(ii)$$

The relationships indicated by eqs. (i) and (ii) are the expressions of *Ostwald's dilution law for weak electrolytes*.

Note. The expression (i) refers only to binary electrolytes, AB. Different expressions must be derived for other electrolytes of the types AB₂, A₂B etc. using the law of equilibrium.

- 4. Ionic-product of water, K_w .** Even the purest water is an electrolyte because of its feeble ionization due to autoprotolysis.



The degree of ionization of water is 18×10^{-10}

$$H^+(aq) \approx OH^-(aq) = \frac{1000}{18} \times 18 \times 10^{-10} = 10^{-7} \text{ mol/litre}$$

The ionic-product of water (K_w) is therefore :

$$K_w = [H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14} \text{ mol}^2/\text{litre}^2 \text{ at } 25^\circ\text{C}$$

- 5. Ionic-product and temperature.** It increases with temperature but the value 10^{-14} is convenient for general calculations.

| | | | | |
|-------|------------------------|-----------------------|------------------------|------------------------|
| T°C | 18 | 25 | 40 | 75 |
| K_w | 0.61×10^{-14} | 1.0×10^{-14} | 2.92×10^{-14} | 16.9×10^{-14} |

- 6. K_w is a constant at a given temperature.** When an acid or a base is added to water, $[H^+]$ and $[OH^-]$ concentrations adjust themselves to an extent that the product $[H^+][OH^-]$ is always a constant at a given temperature, i.e., 1.0×10^{-14} at 25°C .
- 7. (i) pH of a solution.** It is the logarithm of the reciprocal of hydrogen ions concentrations present in the solution in moles per litre.

$$pH = \log \frac{1}{[H^+]} = -\log [H^+]$$

(ii) pOH of a solution. It is the logarithm of the reciprocal of hydroxide ion concentration present in solution in moles per litre.

$$pOH = \log \frac{1}{[OH^-]} = -\log [OH^-]$$

(iii) The pH of neutral solution is 7.0, that of an acidic solution is less than 7 and of the basic solution is more than 7.

Neutral solution ($pH = 7$) ; $[H^+] = [OH^-] = 10^{-7}$

Acidic solution ($pH < 7$) ; $[H^+] > [OH^-]$

Basic solution ($pH > 7$) ; $[H^+] < [OH^-]$



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$$[H^+] = 10^{-8} M + \frac{10^{-14}}{[H^+]} \quad (\because [Cl^-] = 10^{-8} M)$$

or $[H^+]^2 - 10^{-8} [H^+] - 10^{-14} = 0$

Solving the quadratic equation and taking the positive

$$\therefore [H^+] = 1.051 \times 10^{-7} M$$

$$pH = -\log [H^+] \approx 6.98$$

Problem 8. What is the *pH* of $10^{-8} M$ NaOH solution ?

Solution. $10^{-8} M$ NaOH is a very dilute solution and the contribution of OH^- ions due to self-ionization of water cannot be neglected.

$$\begin{aligned} [OH^-]_{\text{total}} &= [OH^-]_{\text{NaOH}} + [OH^-]_{\text{H}_2\text{O}} \\ &= 10^{-8} M + [OH^-]_{\text{H}_2\text{O}} \end{aligned}$$

$$[H^+] [OH^-] = 10^{-14}$$

$$[H^+]_{\text{H}_2\text{O}} (10^{-8} + [OH^-]_{\text{H}_2\text{O}}) = 10^{-14}$$

Since, $[H^+]_{\text{H}_2\text{O}} = [OH^-]_{\text{H}_2\text{O}}$

$$\therefore [OH^-]_{\text{H}_2\text{O}} (10^{-8} + [OH^-]_{\text{H}_2\text{O}}) = 10^{-14}$$

$$[OH^-]_{\text{H}_2\text{O}}^2 + 10^{-8} [OH^-]_{\text{H}_2\text{O}} - 10^{-14} = 0$$

Use quadratic equation to solve it.

$$[OH^-]_{\text{H}_2\text{O}} = 9.5125 \times 10^{-8} M$$

$$\begin{aligned} [OH^-]_{\text{total}} &= [OH^-]_{\text{NaOH}} + [OH^-]_{\text{H}_2\text{O}} \\ &= 10^{-8} M + 9.5125 \times 10^{-8} M \\ &= 1.051 \times 10^{-7} \end{aligned}$$

$$[H^+] [OH^-] = 10^{-14}$$

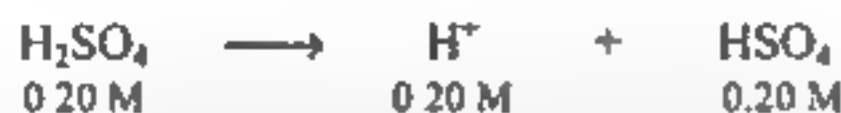
$$\begin{aligned} H^+ &= \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{1.051 \times 10^{-7}} \\ &= 9.515 \times 10^{-8} M \end{aligned}$$

$$\begin{aligned} pH &= -\log [H^+] = -\log 9.515 \times 10^{-8} \\ &= 7.0216 \approx 7.02 \end{aligned}$$

Problem 9. Calculate the *pH* of $0.20 M$ H_2SO_4 .



Solution. The very high value of K_1 indicates that the first step goes 100 percent to the right.



The small value of K_2 indicates that only a part of HSO_4^- ionizes to give H^+ and SO_4^{2-} . Let the number of moles of H^+ generated in the second step be x mol/litre

$$[H^+] = 0.20 + x \text{ mol/litre}$$

$$[HSO_4^-] = 0.20 - x \text{ mol/litre}$$

$$[SO_4^{2-}] = x \text{ mol/litre}$$



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PROBLEMS FOR PRACTICE

1. A 0.1 M formic acid solution is 4.24% ionized at 25°C. What is the ionization constant for formic acid?
2. The pH of a 0.1 M solution of an organic acid is 3.0. Calculate the dissociation constant of the acid.
3. The pH of 0.0022 M HNO_2 solution is 1.0. What is the value of ionization constant for HNO_2 ?
4. The degree of dissociation of a 0.2 M chloroacetic acid solution at 25°C is 0.00088. What is K_a for chloro-acetic acid?
5. The dissociation constant of formic acid is 1.8×10^{-4} . Calculate the percentage degree of ionization of 10^{-5} M formic acid solution using the relationship $K_a \approx C\alpha^2$. Why is the answer you get absurd? What is the correct answer?
6. The degree of ionization of a weak monobasic acid in 0.1M solution is 0.0133. What will be the degree of ionization of this acid in 0.01M solution?
7. What is pH and pOH of 0.02 M HCl solution?
8. What is the pH of 0.5 M formic acid?
9. The pH of a soft drink is 3.82. Find the hydrogen ion concentration.
10. Ionization-constant for acetic acid is 1.8×10^{-5} . What is the pH of a 0.01 M acetic acid solution?
11. What is the hydroxyl ion concentration of a solution containing 0.1 mole NH_3 per litre? K_b for NH_3 is 1.8×10^{-5} .
12. What are the pH and pOH values of a 0.05M NH_3 solution? K_b for NH_3 is 1.8×10^{-5} .
13. What is the degree of ionization of a 0.2 M NH_2OH solution? K_b for NH_2OH is 1.1×10^{-8} .
14. A 0.05 M methylamine solution is 10% ionized. What is the dissociation constant of methylamine?
15. What is the pH of 0.01 M sodium hydroxide solution at 25°C if the ionic product of water at that temperature is $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$?
16. (a) What is the approximate pH of 1×10^{-7} M HCl ?
(b) What is the correct pH of 1×10^{-7} M HCl ?
17. (a) What is the approximate pH of 1×10^{-7} M $NaOH$?
(b) What is the correct pH of 1×10^{-7} M $NaOH$?
18. Calculate the pH of 6.0×10^{-7} M HCl taking into account the contribution of H_3O^+ ions due to self-ionization of water.
19. Calculate the pH of 6.0×10^{-7} M $NaOH$ taking into account the contribution of H_3O^+ ions due to self-ionization of water.
20. Calculate the pH of 0.10 M H_2SO_4
 Given : $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ $K_1 \geq 1$
 $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $K_2 = 1.26 \times 10^{-2}$



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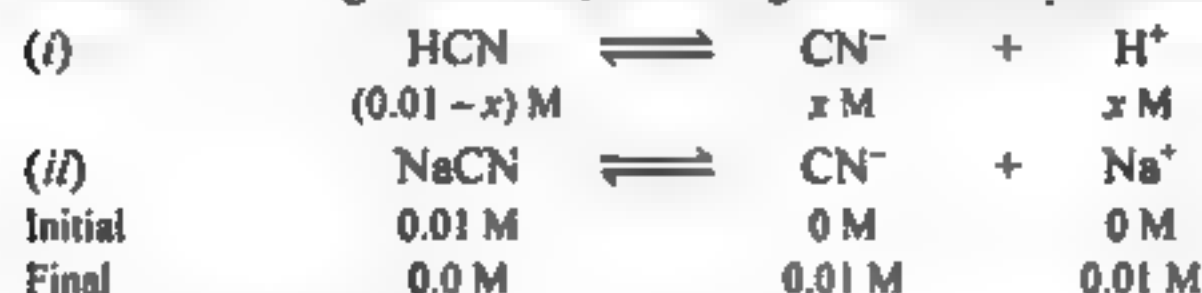
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Problem 14. The concentration of HCN and NaCN in a solution is 0.01M each. Calculate the concentration of hydrogen and hydroxyl ions if the dissociation constant of HCN is 7.2×10^{-10} . (Roorkee 1991)

Solution. In the given buffer, following reactions occur simultaneously :



\therefore At equilibrium, $[\text{H}^+] = x \text{ m}$

$$[\text{CN}^-]_{\text{Total}} = [\text{CN}^-]_{\text{acid}} + [\text{CN}^-]_{\text{salt}}$$

$$= x \text{ M} + 0.01 \text{ M} \approx 0.01 \text{ M}$$

$$[\text{HCN}] = 0.01 \text{ M} - x \text{ M} \approx 0.01 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CN}^-]}{[\text{HCN}]}$$

$$= -\log 7.2 \times 10^{-10} + \log \frac{1.01 \text{ M}}{0.01 \text{ M}}$$

$$-\log [\text{H}^+] = \log 7.2 \times 10^{-10}$$

$$[\text{H}^+] = 7.2 \times 10^{-10} \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{7.2 \times 10^{-10}} = 1.4 \times 10^{-5} \text{ M}$$

Problem 15. What volume of 0.10 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH 4.0 ? $\text{p}K_a$ for formic acid is 3.80. (Roorkee 1990)

Solution. Let the volume added of 0.10 M sodium formate solution be V mL.

$$\text{Total volume of the buffer} = (50 + V) \text{ mL}$$

$$\text{Molarity of formate ion in the buffer} = \frac{0.1 \text{ M} \times V}{(50 + V)}$$

$$\text{Molarity of formic acid in the buffer} = \frac{0.05 \text{ M} \times 50}{(50 + V)}$$

Using Handerson equation :

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$\log \frac{[\text{HCOO}^-]}{[\text{HCOOH}]} = \text{pH} - \text{p}K_a$$

$$\log \frac{0.1 \text{ M} \times V}{(50 + V)} \times \frac{(50 + V)}{0.05 \text{ M} \times 50} = 4.0 - 3.80$$

$$\log (0.04 V) = 0.20$$

$$0.04 V = \text{Antilog } 0.20 = 1.585$$

$$V = \frac{1.585}{0.04} = 39.63 \text{ mL}$$



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$$\begin{aligned}
 [\text{Ag}^+] &= \frac{K \times [\text{Ag}(\text{CN})_2]^-}{[\text{CN}^-]^2} \\
 &= \frac{4.0 \times 10^{-19} \times 0.03 \text{ M}}{(0.04)^2} = 7.5 \times 10^{-18} \text{ M}
 \end{aligned}$$

Problem 20. 0.15M of pyridinium chloride has been added into 500 cm³ of 0.3M pyridine solution. Calculate *pH* and hydroxyl ion concentration in the resulting solution assuming no change in volume. (*K_b* for pyridine = 1.5 × 10⁻⁹ M)

(Roorkee 1995)

Solution. For an alkaline buffer :

$$pH = pK_w - pK_b + \log \frac{\text{Base}}{\text{Salt}}$$

$$\text{Pyridine (Base)} = 0.2 \text{ M}$$

$$\text{Pyridinium chloride} = 0.15 \text{ mole} \times \frac{1000 \text{ cm}^3}{500 \text{ cm}^3} = 0.3 \text{ M}$$

$$pH = 14 - (-\log K_b) + \log \frac{0.2 \text{ M}}{0.3 \text{ M}}$$

$$= 14 - (-\log 1.5 \times 10^{-9}) + \log \frac{0.2 \text{ M}}{0.3 \text{ M}}$$

$$= 14 - 8.8239 - 0.1761 = 5$$

$$[\text{H}^+] = 10^{-pH} = 1.0 \times 10^{-5}$$

$$[\text{H}^+][\text{OH}^-] = K_w$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9} \text{ M.}$$

Problem 21. Calculate the amount of NH₃ and NH₄Cl required to prepare a buffer solution of *pH* 9.0 when total concentration of buffering reagents is 0.6 mol L⁻¹. (*pK_b* for NH₃ = 4.7, log 2 = 0.30)

(Roorkee 1997)

Solution. $pOH = 14 - pH = 14 - 9.0 = 5$

$$pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$5 = 4.7 + \log \frac{a}{b}$$

$$\frac{a}{b} = \text{Antilog } 0.30 = 2$$

or $a = 2b$

Given, $a + b = 0.6 \text{ M}$

$$2b + b = 0.6$$

$$b = 0.2 \text{ M}$$

$$a = 0.6 \text{ M} - 0.2 \text{ M} = 0.4 \text{ M}$$

$$\text{Amount of salt} = 0.4 \text{ M} \times \text{Eq. Mass of NH}_4\text{Cl} = 0.4 \times 53.5 = 21.4 \text{ g/L}$$

$$\text{Amount of NH}_3 = 0.2 \text{ M} \times \text{Eq. Mass of NH}_3 = 0.2 \times 17 = 3.4 \text{ g/L}$$



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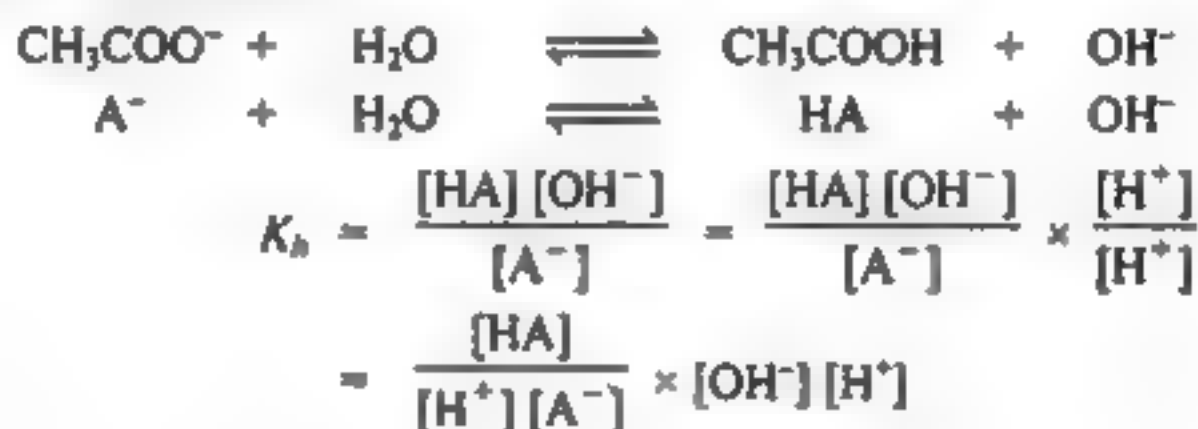
Hydrolysis

- 1. Hydrolysis.** It is a reaction in which an ion, formed by dissolving a salt in water, reacts with water to form acidic or alkaline solution. It is a reversible reaction which contains ionized as well as unionized species.
- 2. Salt of a strong acid and a strong base.** It is not hydrolysed in water and the solution is neutral with a pH of 7. For example, on adding $NaCl$ to water, two reactions occur.



Both $NaOH$ and HCl are completely dissociated in aqueous solution and so produce H^+ and OH^- in equal concentrations. Therefore, the solution does not have excess H^+ or OH^- ions.

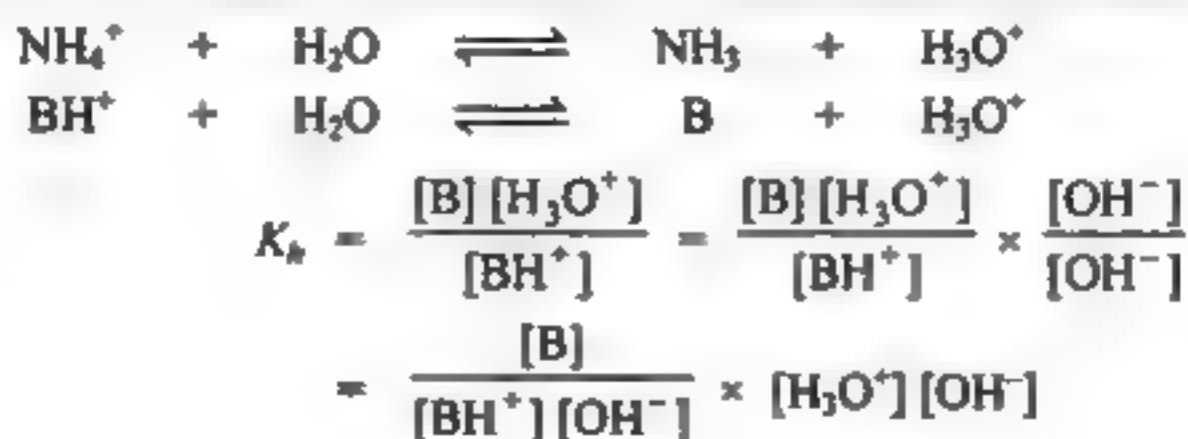
- 3. Anionic hydrolysis.** *Salt of a weak acid and a strong base.* When such a salt (CH_3COONa , $NaCN$ etc.) is dissolved in water, the anion of the weak acid reacts with water to increase the concentration of OH^- ions. The formation of OH^- ions makes the solution alkaline.



$$\boxed{K_h = \frac{K_w}{K_a}}$$

where K_h is called the *hydrolysis constant*, K_a is dissociation constant of the conjugate acid, HA and K_w is the ionic product of water.

- 4. Cationic hydrolysis.** *Salt of a strong acid and weak base.* When such a salt (NH_4Cl) is dissolved in water, the cation of the weak base reacts with water to increase the concentration of H^+ ions. The formation of H^+ ions makes the solution acidic.





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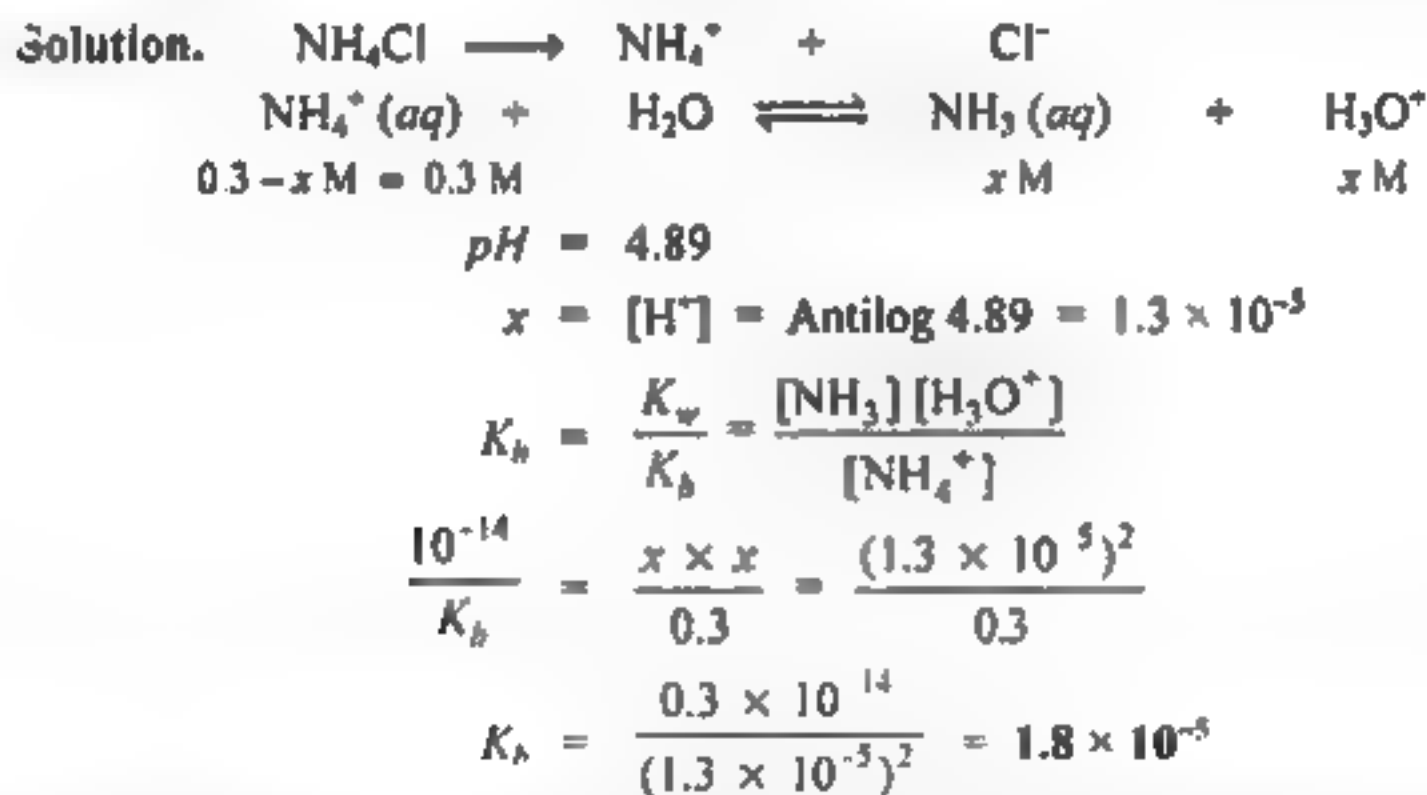
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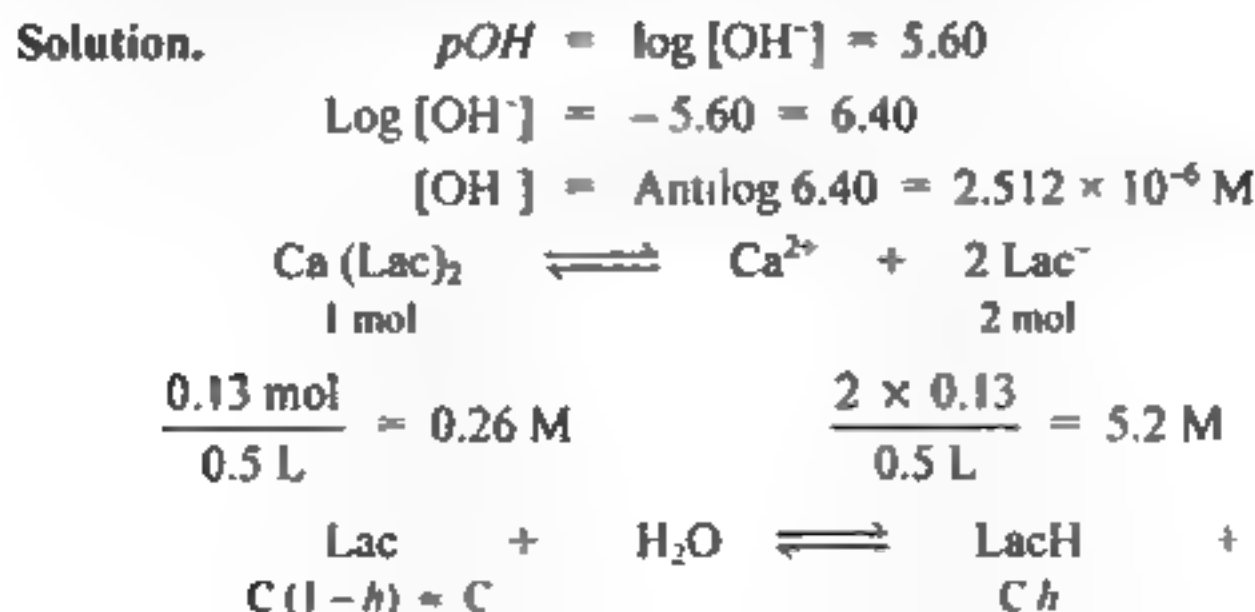
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$$\begin{aligned}
 &= \sqrt{0.77} = 0.877 \\
 \text{(iii)} \quad K_h &= \frac{K_w}{K_a K_b} = \frac{10^{-14}}{7.2 \times 10^{-10} \times 1.8 \times 10^{-5}} = 0.77 \\
 h &= \sqrt{K_h} = \sqrt{0.77} = 0.877 \\
 K_h &= \frac{h^2}{(1-h)^2} \\
 \sqrt{K_h} &= \frac{h}{1-h} = 0.877 \\
 h &= 0.877 - 0.877 h \\
 1.877 h &= 0.877 \\
 h &= \frac{0.877}{1.877} = 0.467
 \end{aligned}$$

Problem 6. The *pH* of a 0.3 M solution of NH_4Cl is 4.89. What is the dissociation constant of NH_3 ?



Problem 7. Calcium lactate is a salt of a weak organic acid and represented as $\text{Ca}(\text{Lac})_2$. A saturated solution of $\text{Ca}(\text{Lac})_2$ contains 0.13 mol of this salt in 0.50 litre solution. The *pOH* of this solution is 5.60. Assuming complete dissociation of the salt, calculate K_a of Lactic acid. (Roorkee 1991)





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Solubility Product

1. In an aqueous solution of a sparingly soluble ionic compound, there exists a *dynamic equilibrium* between the undissolved salt and the ions in solution. For the sparingly soluble silver chloride solid :



$$K_{eq} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

As the concentration of the solid is constant, (saturated solution)

$$K_{sp} = \text{solubility product} = [\text{Ag}^+][\text{Cl}^-]$$

2. **Solubility product expression.** The solubility product of a salt in equilibrium with its ions in a saturated solution is the product of equilibrium concentrations of the ions, each concentration being raised to a power equal to the coefficient in the balanced equation.

In general for the electrolyte $A_x B_y$:



$$\text{Solubility product} = K_{sp} (A_x B_y) = [A^{n+}]^x [B^{m-}]^y$$

Examples :



$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$



$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$



$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$



$$K_{sp} = [\text{Mg}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

3. **Ionic product.** In an aqueous solution of an electrolyte, the product of concentrations of the ions, each concentration being raised to a power equal to the coefficient in the balanced equation, is called the *ionic product*.
4. The solubility of a sparingly soluble ionic solid can be calculated from its solubility product value and vice-versa.



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PROBLEMS FOR PRACTICE

1. The concentrations of lead ions and iodide ions in a saturated solution of lead iodide are 1.28×10^{-3} M and 5.6×10^{-3} M respectively. What is the solubility product of lead iodide?
2. The solubility of MgF_2 at 298 K is 0.13 g/litre. What is the solubility product of MgF_2 ?
3. The solubility of calcium carbonate in pure water is 0.00093 gram per 100 mL at 25°C . What is the solubility product constant of calcium carbonate?
4. The solubility product of lead sulphate at 25°C is 1.3×10^{-8} . What is the solubility of lead sulphate at 25°C ?
5. What is the solubility of lead chloride in grams per 100 mL solution if the solubility product of lead chloride is 1.01×10^{-6} ?
6. The solubility product of $\text{Fe}(\text{OH})_3$ is 1×10^{-36} . What is the solubility of ferric hydroxide in grams per litre?
7. The solubility product of Ag_2CrO_4 is 1.9×10^{-12} . What is the solubility of Ag_2CrO_4 ?
8. All the hardness in a tap water supply consists of sulphate ions and the system is saturated with CaSO_4 at 25°C . If the SO_4^{2-} concentration is 6.5×10^{-2} M, what is the calcium ion concentration in water? The solubility product of CaSO_4 is 2.4×10^{-5} .
9. A solution contains sodium chloride only. Sufficient silver nitrate is added into it to make the solution 0.2 M in Ag^+ (aq). What concentration of Cl^- ions remain in solution? K_{sp} of AgCl is 1.8×10^{-10} .
10. Sufficient sodium carbonate solution is added into an aqueous copper sulphate solution to make it 0.1 M in CO_3^{2-} ions. What concentration of Cu^{2+} ions remain in solution? The solubility product of CuCO_3 is 2.5×10^{-10} .
11. The solubility product of silver oxalate is 1.1×10^{-11} . Will a precipitate of silver oxalate form when 10 mL of 1×10^{-3} M AgNO_3 is mixed with 10 mL of 1×10^{-4} M sodium oxalate solution?
12. The solubility product of calcium iodate is 6.4×10^{-9} . How many milligram of the salt can be dissolved in 500 mL of water?
13. If each mL of a saturated solution of K_2PtCl_6 contains 11 mg of the salt, calculate its solubility product. $\text{Pt} = 195$.
14. A solution is saturated with respect to BaF_2 , $K_{sp} = 1.0 \times 10^{-6}$ and BaSO_4 , $K_{sp} = 1.3 \times 10^{-10}$. If $[\text{F}^-]$ is 7.5×10^{-4} M, calculate $[\text{SO}_4^{2-}]$.

ANSWERS

- | | | |
|----------------------------|---------------------------------|--|
| 1. 6×10^{-7} | 2. 3.7×10^{-8} | 3. 8.6×10^{-9} |
| 4. 1.14×10^{-4} M | 5. 0.175 g | 6. 4.7×10^{-10} g L^{-1} |
| 7. 7.8×10^{-5} M | 8. 3.7×10^{-4} M | 9. 9×10^{-10} M |
| 10. 2.5×10^{-9} | 11. Yes; 1.25×10^{-11} | 12. 228 mg |
| 13. 4.6×10^{-3} | 14. 7.3×10^{-11} M | |



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$$\% \text{ of } [\text{Ag}^+] \text{ that remains unprecipitated} = \frac{1.7 \times 10^{-4}}{0.1} \times 100 = 0.17\%$$

$$\text{Hence, \% of } [\text{Ag}^+] \text{ precipitated} = 100 - 0.17 = 99.83\%.$$

Problem 4. A solution contains a mixture of barium ions, $[\text{Ba}^{2+}] = 0.1 \text{ M}$ and strontium ions $[\text{Sr}^{2+}] = 0.1 \text{ M}$. Both the ions are precipitated down by adding sodium sulphate. Calculate the $[\text{SO}_4^{2-}]$ at which barium just begin to precipitate. Calculate the concentration of barium ions remaining in solution when SrSO_4 just begins to precipitate. The solubility products of BaSO_4 and SrSO_4 are 1.1×10^{-10} and 2.8×10^{-7} respectively.



$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = \frac{K_{sp}}{[\text{Ba}^{2+}]} = \frac{1.1 \times 10^{-10}}{0.1 \text{ M}} = 1.1 \times 10^{-9} \text{ M}$$

When $[\text{SO}_4^{2-}] = 1.1 \times 10^{-9} \text{ M}$, BaSO_4 starts precipitating.



$$K_{sp} = [\text{Sr}^{2+}][\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = \frac{K_{sp}}{[\text{Sr}^{2+}]} = \frac{2.8 \times 10^{-7}}{0.1 \text{ M}} = 2.8 \times 10^{-6} \text{ M}$$

SrSO_4 starts precipitating when $[\text{SO}_4^{2-}] = 2.8 \times 10^{-6} \text{ M}$.

$$\therefore [\text{Ba}^{2+}] = \frac{K_{sp}}{[\text{SO}_4^{2-}]} = \frac{1.1 \times 10^{-10}}{2.8 \times 10^{-6}} = 0.000039 \text{ M Ba}^{2+}$$

Alternative Method :

$$\frac{[\text{Ba}^{2+}][\text{SO}_4^{2-}]}{[\text{Sr}^{2+}][\text{SO}_4^{2-}]} = \frac{1.1 \times 10^{-10}}{2.8 \times 10^{-7}}$$

$$\frac{[\text{Ba}^{2+}]}{[\text{Sr}^{2+}]} = 0.00039$$

When $[\text{Sr}^{2+}] = 0.10 \text{ M}$

$$[\text{Ba}^{2+}] = 0.10 \text{ M} \times 0.00039 = 0.000039 \text{ M}.$$

Problem 5. A sample of AgCl was treated with 5.00 mL of $1.5 \text{ M Na}_2\text{CO}_3$ solution to give Ag_2CO_3 . The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl ($K_{sp} \text{ Ag}_2\text{CO}_3 = 8.2 \times 10^{-12}$). (IIT/JEE 1997)



$$K_{sp}(\text{Ag}_2\text{CO}_3) = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$

$$[\text{Ag}^+]^2 = \frac{K_{sp}(\text{Ag}_2\text{CO}_3)}{[\text{CO}_3^{2-}]}$$

when $[\text{CO}_3^{2-}] = 1.5 \text{ M}$



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PROBLEMS FOR PRACTICE

1. How many moles of AgBr will dissolve in a 0.01 M NaBr solution. K_{sp} of AgBr is 5×10^{-13} and NaBr dissociates completely in water.
2. A solution is 0.1M in NaF. Excess solid lead fluoride is added. What will be Pb^{2+} concentration at equilibrium? K_{sp} of PbF_2 is 4×10^{-8} .
3. The solubility of barium chromate at 25°C is 2.337×10^{-4} g/100 mL. Calculate its solubility (in g/litre) in 0.01 M barium chloride solution.
4. K_{sp} of $Cd(OH)_2$ is 2.0×10^{-14} . What is the solubility of $Cd(OH)_2$ in 0.05 $Cd(NO_3)_2$ solution in g/100 ml solution?
5. A solution is 0.05 M in $Zn(NO_3)_2$. Excess solid $ZnCO_3$ is added. What will be the $[CO_3^{2-}]$ at equilibrium. K_{sp} of $ZnCO_3$ is 2.0×10^{-10} .
6. A solution contains 0.1M KCl and 0.1M K_2CrO_4 . The anions Cl^- and CrO_4^{2-} are to be separated by selective precipitation. If the concentration of $[Ag^+]$ is increased by adding solid $AgNO_3$ gradually, which will first precipitate? What is the percentage of Cl^- that remains in solution when Ag_2CrO_4 just begins to precipitate? $K_{sp} : AgCl = 1.7 \times 10^{-10}$; $Ag_2CrO_4 = 1.9 \times 10^{-12}$.
7. A solution contains 0.10 M $Zn(NO_3)_2$ and 0.0010 M $Cd(NO_3)_2$. Zn^{2+} and Cd^{2+} are to be separated as sulphides by selective precipitation. Hydrogen sulphide gas is passed through this solution and $[S^{2-}]$ concentration is gradually increased by increasing the pH of the solution. What percentage of Cd^{2+} ions remains unprecipitated at a concentration at which Zn^{2+} just begins to precipitate as sulphide? $K_{sp} : CdS = 7 \times 10^{-27}$; $ZnS = 1.6 \times 10^{-23}$.
8. A solution is 0.2M in Fe^{2+} and 0.2M in Pb^{2+} in an acidic medium. $[OH^-]$ concentration is increased gradually by adding solid NaOH. What percentage of the metal ion that precipitates first as hydroxide remains in solution at a concentration of $[OH^-]$ ions at which the other metal ion just begins to precipitate. $K_{sp} : Pb(OH)_2 = 4.2 \times 10^{-15}$, $Fe(OH)_2 = 2 \times 10^{-15}$.
9. 250 mL of a solution contains 0.20 M Ca^{2+} and 0.20 M Mg^{2+} . How many milligrams of which cation would remain in solution when Na_2CO_3 is added slowly at stage at which the other cation just starts to precipitate. The solubility products of $CaCO_3$ and $MgCO_3$ are 1.7×10^{-8} and 2.6×10^{-5} respectively.
10. Calculate the ratio of $[Br^-]$ and $[Cl^-]$ in a solution in which sufficient $AgNO_3$ has been added to cause precipitation of both the halides. K_{sp} of AgBr = 5.2×10^{-13} ; K_{sp} of AgCl = 1.6×10^{-10} .

ANSWERS

- | | | |
|-----------------------------------|-------------------------|-----------------------------|
| 1. 5×10^{-11} M | 2. 4×10^{-6} M | 3. 2.2×10^{-6} g/L |
| 4. 4.63×10^{-6} g/100 mL | 5. 4×10^{-9} M | 6. 0.039% |
| 7. $6 \times 10^{-3}\%$ | 8. 47.5% Fe^{2+} | 9. 1.3 mg Ca^{2+} |
| 10. 0.00325 | | |



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$$[\text{OH}^-] = \sqrt{\frac{2.0 \times 10^{-16}}{0.01}} = 1.4 \times 10^{-7} \text{ M}$$

$\therefore [\text{OH}^-]$ concentration cannot be more than $1.4 \times 10^{-7} \text{ M}$.



$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = K_{\text{eq}} = 1.8 \times 10^{-5}$$

$$\frac{[\text{NH}_4^+](1.4 \times 10^{-7})}{0.01} = 1.8 \times 10^{-5}$$

$$[\text{NH}_4^+] = \frac{0.01 \times 1.8 \times 10^{-5}}{1.4 \times 10^{-7}} = 1.29 \text{ M.}$$

Problem 4. A solution is 0.04M in Mn^{2+} . What is the pH of the solution at which no precipitate forms when the solution is saturated with H_2S ? The solubility product of MnS is 7×10^{-16} . For a solution saturated with H_2S $[\text{H}^+]^2 [\text{S}^{2-}] = 1.1 \times 10^{-22}$.



$$[\text{Mn}^{2+}][\text{S}^{2-}] = K_{\text{sp}}$$

$$(0.04)[\text{S}^{2-}] = 7 \times 10^{-16}$$

$$[\text{S}^{2-}] = \frac{7 \times 10^{-16}}{0.04} = 1.75 \times 10^{-14} \text{ M}$$

Therefore, $[\text{S}^{2-}]$ must be less than $1.75 \times 10^{-14} \text{ M}$ if MnS is not to precipitate.

For a solution saturated with H_2S ,

$$[\text{H}^+]^2 [\text{S}^{2-}] = 1.1 \times 10^{-22}$$

$$[\text{H}^+]^2 \times (1.75 \times 10^{-14}) = 1.1 \times 10^{-22}$$

$$[\text{H}^+]^2 = \frac{1.1 \times 10^{-22}}{1.75 \times 10^{-14}}$$

$$[\text{H}^+] = \sqrt{\frac{1.1 \times 10^{-22}}{1.75 \times 10^{-14}}} = 7.9 \times 10^{-5} \text{ M}$$

$$pH = -\log [\text{H}^+] = -\log 7.9 \times 10^{-5} = 4.1$$

For a solution with pH less than 4.1, no precipitation will occur.

Problem 5. A solution containing 0.2 M HCl , 0.01 M Hg^{2+} and 0.01 M Fe^{2+} is saturated with H_2S . Which will precipitate: HgS or FeS or both. K_{sp} of HgS is 3×10^{-53} and K_{sp} of FeS is 3×10^{-17} .

Solution. For a saturated solution of H_2S ,

$$[\text{H}^+]^2 [\text{S}^{2-}] = 1.1 \times 10^{-22}$$

The given solution is 0.2 M in H^+ .

$$\therefore (0.2)^2 [\text{S}^{2-}] = 1.1 \times 10^{-22}$$

$$[\text{S}^{2-}] = \frac{1.1 \times 10^{-22}}{(0.2)^2} = 2.75 \times 10^{-21} \text{ M}$$



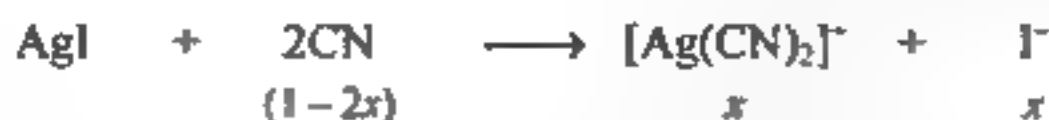
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$$K_{eq} = \frac{x \times x}{(1-2x)^2} = \frac{x^2}{(1-2x)^2} = 8.52 \times 10^2$$

$$\frac{x}{1-2x} = 29.2$$

$$x = 29.2 - 58.4x$$

$$x = 0.49 \text{ moles}$$

Problem 14. The solubility of $\text{Pb}(\text{OH})_2$ in water is $6.7 \times 10^{-6} \text{ M}$. Calculate the solubility of $\text{Pb}(\text{OH})_2$ in a buffer solution of $\text{pH} = 8$. (IIT/JEE 1999)



$$\begin{aligned} K_{sp} \text{ of } \text{Pb}(\text{OH})_2 &= [\text{Pb}^{2+}][\text{OH}^-]^2 = s \times (2s)^2 = 4s^3 \\ &= 4 \times (6.7 \times 10^{-6} \text{ M})^3 = 1.203 \times 10^{-15} \end{aligned}$$

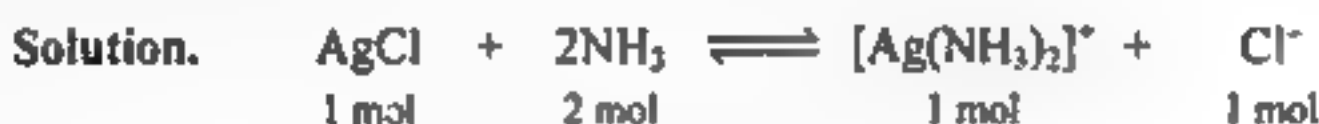
When pH of the solution is 8, then $\text{pOH} = 14 - 8 = 6$

$$[\text{OH}^-] = 10^{-6} \text{ M.}$$

$$[\text{Pb}^{2+}][\text{OH}^-]^2 = K_{sp}$$

$$\begin{aligned} [\text{Pb}^{2+}] &= \frac{K_{sp}}{(\text{OH}^-)^2} = \frac{1.203 \times 10^{-15}}{(10^{-6})^2} \\ &= 1.203 \times 10^{-3} \text{ mol/L} \end{aligned}$$

Problem 15. Determine the concentration of NH_3 solution whose one litre can dissolve 0.10 mole AgCl . K_{sp} of AgCl and K_f of $[\text{Ag}(\text{NH}_3)_2]^+$ are $1.0 \times 10^{-10} \text{ M}^2$ and $1.6 \times 10^7 \text{ M}^{-1}$ respectively. (Roorkee 1999)



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] \quad \dots(i)$$



$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} \quad \dots(ii)$$

Multiplying eq (i) and eq. (ii), one has

$$K_{sp} \times K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+ [\text{Cl}^-]}{[\text{NH}_3]^2}$$

$$\text{or } 1 \times 10^{-10} \times 1.6 \times 10^7 = \frac{a \times a}{[\text{NH}_3]^2}$$

$$\text{Solubility of AgCl} = 0.1 \text{ M}$$

$$\therefore a = 0.1 \text{ M for } [\text{Ag}(\text{NH}_3)_2]^+ \text{ and Cl}$$



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- 7. Faraday's second law of electrolysis.** (a) 1 mole of electrons has a charge of 96500 coulomb.

$$1 \text{ faraday} = 96500 \text{ coulomb}$$

$$1 \text{ faraday} = \text{Movement of 1 mole of electrons } (6.023 \times 10^{23})$$

- (b) 1 mole of ions requires, $96500 \times \text{Number of electrons involved in the reaction}$, electricity for its deposition or liberation.

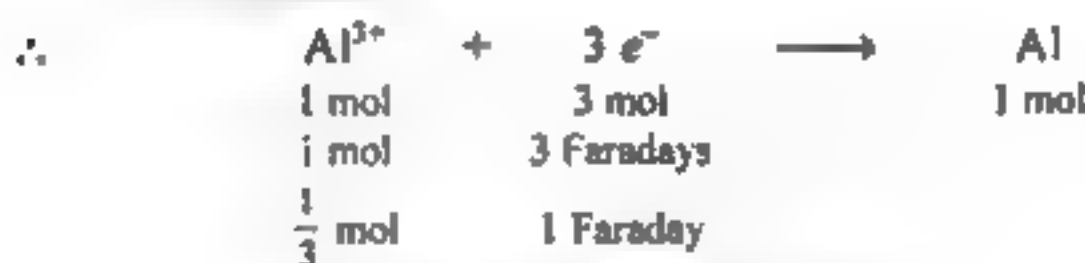
Examples : (i) For a monovalent ion such as Na^+ , Ag^+ , H^+ , etc., the reduction at cathode requires one electron for one positive monovalent ion. Therefore, when one mole of electrons (6.023×10^{23} electrons = 1 faraday = 96500 coulomb) passes through the electrolyte, one mole of the atoms, Na, Ag and H are produced. Or passage of one faraday of electricity produces one gram atomic mass of the monovalent ions, i.e. 1 faraday produces 1 mole of Na atoms (23 g), 1 mole of Ag atoms (107.8 g) and 1 mole of H atoms (1 g).



- (ii) For a bivalent cation, the change at electrode requires two electrons for one bivalent cation.



- (iii) For a trivalent cation, the change at electrode requires three electrons for one trivalent cation.



Therefore, one mole of Al^{3+} requires 3 Faradays.

or 1 Faraday consumes $\frac{1}{3} \text{ mol} = 1$ equivalent mass of Al^{3+} ions.

- 8. On the basis of the discussions in (7) above, Faraday's second law of electrolysis can be stated in the following ways :**

- (a) Integral number of faradays of electricity are required to produce or consume 1 mole of a substance during electrolysis.

Mathematically,

$$\boxed{M = WZF}$$

where Z is the number of electrons involved per ion in the reaction (valency)

Combining it with Faraday's first law of electrolysis,

$$m = WIt, \text{ one has}$$

$$\frac{m}{M} = \frac{It}{ZF} = \frac{Q}{ZF}$$

- (b) Faraday's second law of electrolysis states that the passage of one faraday of electricity produces one chemical equivalent (gram equivalent mass) of a substance.



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Problem 10. What is the volume of oxygen liberated at anode at STP in the electrolysis of CdSO_4 solution when a current of 2 ampere is passed for 8 minutes ? The anode reaction is



Solution.

$$Q = It = 2 \text{ amp} \times 8 \times 60 \text{ sec} \\ = 960 \text{ coulomb}$$

$$Q = \frac{960}{96500} \text{ F}$$

The anode reaction is



4 Faradays produce 1 mole of $\text{O}_2 = 32 \text{ g} = 22.4 \text{ litres at STP}$

$$\begin{aligned} \frac{960}{96500} \text{ F produce} &= \frac{22.4 \text{ L}}{4 \text{ F}} \times \frac{960}{96500} \text{ F} \\ &= 0.056 \text{ litres O}_2 \text{ at STP} \end{aligned}$$

Problem 11. What weight of nickel is plated out in the electrolysis of aqueous nickel sulphate solution that it takes to deposit 2 g of silver in a silver coulometer that is arranged in series with NiSO_4 electrolytic cell ? $\text{Ag} = 107.8 \text{ amu}$, $\text{Ni} = 58.7 \text{ amu}$.

Solution.



107.8 g of Ag (1 mole) is deposited by 1 Faraday

$$2 \text{ g of Ag (1 mole) is deposited by } \frac{1 \text{ F} \times 2 \text{ g}}{107.8}$$

(b) The same amount of electricity passes through the two electrolytic cells because they are arranged in series.



2 Faradays deposit 1 mole of Ni = 58.7 g

$$\frac{2}{107.8} \text{ F deposit} = \frac{58.7 \text{ g}}{2 \text{ F}} \times \frac{2 \text{ F}}{107.8} = 0.5445 \text{ g Ni}$$

Problem 12. A current of 3.5 ampere deposits 0.5 g Na when passed through molten sodium chloride for 10 minutes. What is the electrochemical equivalent of sodium ?

Solution.

$$m = ZIt$$

$$Z = \frac{m}{It}$$

$$\begin{aligned} &= \frac{0.5 \text{ g}}{3.5 \text{ C/sec} \times 10 \times 60 \text{ sec}} \\ &= 0.000238 \text{ g/coulomb} \end{aligned}$$



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voltmeter in series with the electrolytic cell. Calculate the percentage of the theoretical yield of sodium hydroxide obtained. [At. wt. : Cu = 63.6, Na = 23, H = 1, O = 16]. (IIT/JEE 1976)



63.6 g Cu (1 mole) is deposited by 2 Faradays

$$31.8 \text{ g Cu is deposited by} = \frac{2 \text{ F} \times 31.8 \text{ g}}{63.6 \text{ g}} = 1 \text{ F}$$



1 Faraday electricity deposits 1 mole of Na = 23 g

Now,

1 mole Na = 1 mole NaOH

$$23 \text{ g} = 23 + 16 + 1 \text{ g} = 40 \text{ g}$$

According to the definition of normality,

$$1000 \text{ mL of } 1 \text{ N NaOH contain} = 40 \text{ g NaOH}$$

$$\begin{aligned}
 600 \text{ mL of } 1 \text{ N NaOH contain} &= \frac{40 \text{ g} \times 600 \text{ mL}}{1000 \text{ mL}} \\
 &= 24 \text{ g NaOH}
 \end{aligned}$$

$$\text{Theoretical yield} = 40 \text{ g}$$

$$\text{Percentage of the theoretical yield} = \frac{24 \text{ g}}{40 \text{ g}} \times 100 = 60\%$$

Problem 19. Ten grams of a fairly concentrated solution of cupric sulphate is electrolysed using 0.01 Faraday of electricity. Calculate : (IIT/JEE 1976)

(i) the weight of the resulting solution, and

(ii) the number of equivalents of acid or alkali in solution. [At. wt. : O = 16, S = 32, Cu = 63.5]

Solution. Final weight of the solution = Initial weight of the solution – (weight of Cu deposited at cathode + weight of O₂ liberated at anode).

(a) The cathode reaction is :



2 Faradays electricity deposit 1 mole of Cu = 63.5 g

$$0.01 \text{ Faraday electricity deposit} = \frac{63.5 \text{ g}}{2 \text{ F}} \times 0.01 \text{ F} = 0.3175 \text{ g}$$

(b) The anode reaction is :



4 Faradays electricity liberate 1 mole O₂ = 32 g



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17. On passing electric current of a ampere for t hours through acidulated water and solution of copper sulphate, 0.571 g of Cu and 203 mL of hydrogen gas at NTP are liberated. Calculate the equivalent weight of copper.
18. How long a current of 10 ampere has to be passed through a CdSO_4 solution to coat a metal plate of 100 cm^2 with a 0.003 mm thick layer. Density of cadmium is 8.64 g cm^{-3} . Atomic mass of Cd is 112.5 amu.
19. The density of copper is 8.94 g/ml . Find out the number of coulombs needed to plate an area of $10 \text{ cm} \times 10 \text{ cm}$ to a thickness of 10^{-2} cm using copper sulphate solution as the electrolyte. (IIT/JEE 1979)
20. A current of 5.5 ampere is passed for 5 hours between platinum electrodes in 400 mL of a 2.5 M FeCl_3 solution. What will be the molarity of the solution at the end of electrolysis? $\text{Fe} = 56 \text{ g mol}^{-1}$.
21. Following two reactions occur simultaneously at the anode during the electrolysis of dilute aqueous H_2SO_4 .



Following reaction takes place at cathode :



During the electrolysis, 47.3 mL of O_2 gas is evolved at a total pressure of 736 mm Hg at 26°C and 99.64 mL of H_2 gas is evolved at cathode at a total pressure of 738 mm Hg at 26°C . What fraction of anode current is used to form H_2O_2 . Aqueous tension of water at 26°C is 25.21 mm Hg.

22. The electrode reactions for charging of a lead storage battery are



The electrolyte in the battery is an aqueous solution of sulphuric acid. Before charging the sp. gr. of the liquid was found to be 1.11 (15.7% H_2SO_4 by weight). After charging for 100 hours, the sp. gr. of the liquid was found to be 1.28 (36.9% H_2SO_4 by weight). If the battery contained two litres of the liquid, calculate the average current used for charging the battery. Assume that the volume of the battery liquid remained constant during charging. (IIT/JEE 1972)

23. An electric current is passed through a solution of (i) silver nitrate and (ii) a solution of 10 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals in 500 mL water, platinum electrodes being used in each case. After 30 minutes it is found that 1.307 g silver has been deposited. What was the concentration of copper expressed in grams of copper per litre in the copper sulphate solution after electrolysis? (IIT/JEE 1973)
24. Silver is electrodeposited on a metallic vessel of surface area of 800 cm^2 by passing a current of 0.20 ampere for 3.0 hours. Calculate thickness of silver deposited, given its density is 10.47 g/cc . Atomic weight of silver is 107.92. (IIT/JEE 1978)
25. An electrolytic bath contains chromium (III) nitrate solution and a copper cathode with an area of 256 cm^2 . Calculate the time required to deposit a 0.103 mm thick layer of chromium on copper by passing a current of 3.61 amperes. The current efficiency for the formation of chromium is 75.3% and density of chromium is 7.2 g/cm^3 .



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(b) Note their reduction electrode potential, $E_{M^{n+}/M}$

(c) If oxidation electrode potential is given, change it to reduction electrode potential.

$$E_{\text{red}} = -E_{\text{oxd.}}$$

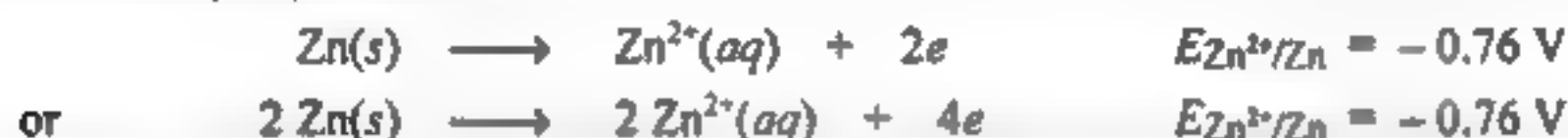
| | |
|-----|--|
| (d) | $\begin{aligned} \text{Cell potential} &= \text{Reduction electrode potential (cathode)} - \text{Reduction electrode potential (anode)} \\ &= E_{\text{red (cathode)}} - E_{\text{red (anode)}} \end{aligned}$ |
|-----|--|

For Daniel cell, $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

$$\begin{aligned} \text{Cell potential} &= E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.34 - (-0.76) \\ &= +0.34 + 0.76 = +1.10 \text{ V} \end{aligned}$$

A cell reaction takes place only when the cell-potential is positive. If it is negative, the reaction takes place in the reverse direction.

12. The electrode potential of an electrode remains the same even if we multiply a half-reaction by any number.



13. Nernst equation. This equation is used to find out the electrode potential of an electrode in which the concentration of metal ions in solution is not 1 M, i.e., at a concentration of $[M^{n+}]$.

For $M^{n+} + ne^- \longrightarrow M$

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

where, E = Reduction electrode potential

E° = Standard reduction electrode potential

n = Number of electrons involved in the balanced equation of the half-reaction.

$[M]$ = Molar concentration or activity of the metal. It is always unity (1).

$[M^{n+}]$ = Molar concentration or activity of the ions.

R = Gas constant, $8.3143 \text{ JK}^{-1} \text{ mol}^{-1}$

T = Temperature in Kelvin

F = Faraday constant = 96500 coulomb

At 25°C (298 K),

$$\begin{aligned} E &= E^\circ - \frac{2.303 \times 8.3143 \times 298}{n \times 96500} \log \frac{1}{[M^{n+}]} \\ &= E^\circ - \frac{0.05916}{n} \log \frac{1}{[M^{n+}]} \end{aligned}$$

For a half-cell involving a gas, the activity of the gas is equal to the partial pressure of the gas in atmospheres.



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$$\begin{aligned}
 &= [-0.14 - (-0.76)] - \frac{0.05916}{2} \log \frac{0.10}{0.001} \\
 &= +0.62 - \frac{0.05916}{2} \log 100 = 0.56 \text{ V}
 \end{aligned}$$

Problem 12. What is the potential for the cell :



$$E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}; \quad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$

Solution. *Anode Half-reaction :*



or



or



$$n = 6$$

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.05916}{n} \log Q$$

$$= E^\circ_{\text{Fe}^{2+}/\text{Fe}} - E^\circ_{\text{Cr}^{3+}/\text{Cr}} - \frac{0.05916}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

$$= -0.44 - (-0.74) - \frac{0.05916}{6} \log \frac{(0.10)^2}{(0.01)^3}$$

$$= 0.3 - \frac{0.05916}{6} \log 10^4$$

$$= 0.3 - 0.0394 \text{ V} = +0.2606 \text{ V} = 0.26 \text{ V}$$

Problem 13. What is the potential for the cell :



$$E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}; \quad E^\circ_{\frac{1}{2}\text{Cl}_2/\text{Cl}^-} = +1.36 \text{ V}$$

Solution. *Anode Half-reaction :*



or *Cathode Half-reaction :*



The cell-reaction is



The value of n is 2.

$$Q = \frac{[\text{Ag}^+]^2 [\text{Cl}^-]^2}{[\text{Cl}_2]}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.05916}{n} \log Q$$

$$= E^\circ_{\frac{1}{2}\text{Cl}_2/\text{Cl}^-} - E^\circ_{\text{Ag}^+/\text{Ag}} - \frac{0.05916}{2} \log \frac{[\text{Ag}^+]^2 [\text{Cl}^-]^2}{[\text{Cl}_2]}$$



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$$\log \frac{C_1}{C_2} = \frac{0.118 \text{ V}}{0.0591} = 2$$

$$\frac{C_1}{C_2} = \text{Antilog } 2 = 10^2$$

$$C_1 = C_2 \times 10^2 = 10^{-6} \text{ M} \times 10^2 = 10^{-4} \text{ M}$$

Problem 21. The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard e.m.f. is positive. For what concentration of Ag^+ will the e.m.f. of the cell, at 25°C , be zero if the concentration of Cu^{2+} is 0.01 M ? (IIT/JEE 1990)

Solution. $\text{Cu}^{2+}/\text{Cu} \parallel \text{Ag}^+/\text{Ag}$

Anode Half-reaction : $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^-$

Cathode Half-reaction : $2\text{Ag}^+ + 2e^- \longrightarrow 2\text{Ag}$

Cell-reaction : $\text{Cu} + 2\text{Ag}^+ \longrightarrow \text{Cu}^{2+} + 2\text{Ag}$

The value of n is 2.

$$Q = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.01 \text{ M}}{[\text{Ag}^+]^2}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.05916}{n} \log Q$$

$$0 \text{ V} = (0.799 \text{ V} - 0.337 \text{ V}) - \frac{0.05916}{2} \log Q$$

$$\log Q = \frac{0.462 \times 2}{0.05916} = 15.6187$$

$$Q = \text{Antilog } 15.6187 = 4.158 \times 10^{15}$$

$$\frac{0.01 \text{ M}}{[\text{Ag}^+]^2} = 4.158 \times 10^{15}$$

$$[\text{Ag}^+]^2 = \frac{0.01}{4.158 \times 10^{15}} = 2.4 \times 10^{-18}$$

$$[\text{Ag}^+] = \sqrt{2.4 \times 10^{-18}} = 1.55 \times 10^{-9} \text{ M}$$

Problem 22. Zinc granules are added in excess to a 500 mL of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of Zn^{2+}/Zn and Ni^{2+}/Ni are -0.75 V and -0.24 V respectively, find out the concentration of Ni^{2+} in solution at equilibrium. (IIT/JEE 1991)

Solution.

| | | | | | | |
|-------------|---|------------------|-------------------|------------------|---|-------------|
| Zn | + | Ni^{2+} | \longrightarrow | Zn^{2+} | + | Ni |
| 1 mol | | 1 mol | | 1 mol | | 1 mol |

Anode Half-reaction : $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$

Cathode Half-reaction : $\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$ $\therefore n$ is equal to 2.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= -0.24 \text{ V} - (-0.75 \text{ V}) = +0.51 \text{ V} \end{aligned}$$



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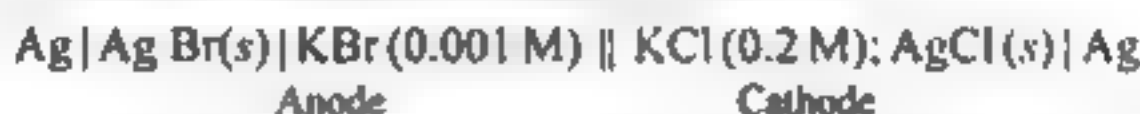


$$Q = \frac{[\text{Ag}^+(\text{AgCl})]}{[\text{Ag}^+(\text{AgBr})]} = \frac{14 \times 10^{-10} \text{ M}}{3.3 \times 10^{-10} \text{ M}} = \frac{14}{3.3}$$

or $\log Q = \frac{14}{3.3} = 0.6276$

$$E = E^\circ_{\text{cell}} - \frac{0.059}{n} \log Q = 0 - \frac{0.059}{1} \times 0.6276 \\ = -0.037 \text{ V}$$

The minus value of cell-potential (-0.037 V) indicates that the cell-reaction occurs in the opposite direction and the cell should therefore be written as



Problem 13. The standard reduction potential at 25°C of the reaction,



is -0.8277 V . Calculate the equilibrium constant for the reaction $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ at 25°C . (IIT/JEE 1989)



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ = -0.8277 \text{ V} - (0 \text{ V}) = -0.8277 \text{ V}$$

$$\log K = \frac{n F E^\circ}{2.303 RT} \\ = \frac{1 \times 96500 \text{ C mol}^{-1} \times (-0.8277 \text{ V})}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = -13.9985$$

$$K = \text{Antilog } -13.9985 = 1.00 \times 10^{-14}$$

Problem 14. The standard reduction potential for the half-cell



is 0.78 V .

(IIT/JEE 1993)

(i) Calculate the reduction potential in 8 M H^+ .

(ii) What will be the reduction potential of the half-cell in a neutral solution ?

Assume all the other species to be at unit concentration.



$$Q = K_c = \frac{[\text{NO}_2][\text{H}_2\text{O}]}{[\text{NO}_3^-][\text{H}^+]^2} \\ = \frac{1}{[\text{H}^+]^2} = \frac{1}{8^2} = \frac{1}{64} \quad \left[\begin{array}{l} \text{NO}_3^- = 1 \text{ M, NO}_2 = 1 \text{ atm} \\ [\text{H}_2\text{O}] = \text{Constant} \end{array} \right]$$



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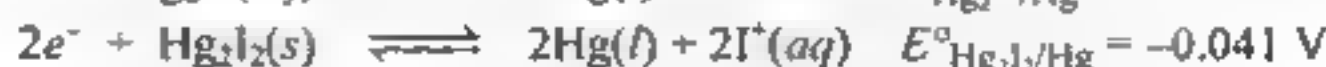


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8. Calculate the solubility product of
- Hg_2I_2
- from the electrode potentials



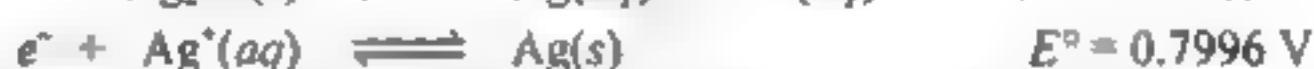
9. The e.m.f. of the cell
- $\text{Hg}(\text{l}) | \text{Hg}_2\text{Cl}_2(\text{s}) | 0.1 \text{ M KCl} || \text{Hg}_2^{2+} (0.1 \text{ M}) | \text{Hg}(\text{l})$
- is 0.44 V at
- 25°C
- . Calculate the solubility product of
- Hg_2Cl_2
- at
- 25°C
- .

10. Calculate the standard potential, the standard free energy and equilibrium constant for the reaction :



$$E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V} ; \quad E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

11. Calculate the solubility product of
- AgBr
- from the following data :



12. The solubility product value of
- $\text{Zn}(\text{OH})_2$
- is
- $1.8 \times 10^{-14} \text{ M}^3$
- . Calculate
- E°
- for the half-cell reaction



13. The solubility product of
- CuI
- is
- $1.1 \times 10^{-12} \text{ M}^2$
- . Calculate the cell-potential for the cell,



14. Calculate the e.m.f. and
- ΔG
- of the cell-reaction for the following cell at
- 25°C
- :



$$E^\circ \text{ values : } \text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V} ; \text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V} ; F = 96500 \text{ coulomb mol}^{-1}.$$

(CBSE 2000)

ANSWERS

1. (a) -212 kJ ; (b) $-17 \text{ JK}^{-1} \text{ mol}^{-1}$; (c) 2×10^{-37}

2. (a) -119660 J ; (b) 8.83×10^{20} .

3. (a) -474780 J ; (b) 1.28×10^{21}

4. 9.7×10^{13}

5. (a) -0.197 V ; (b) $+1.56 \text{ V}$

6. $-116 \text{ JK}^{-1} \text{ mol}^{-1}$

7. $+66 \text{ JK}^{-1} \text{ mol}^{-1}$

8. 9.1×10^{-29}

9. 1.36×10^{-16}

10. (a) 0.02 V ; (b) -12000 J ; (iii) 1×10^2

11. 4.82×10^{-13}

12. -1.17 V

13. 0.71 V

14. $E^\circ = 2.68 \text{ V}$, $\Delta G^\circ = -517240 \text{ J}$



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$$\begin{aligned} K_a &= \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \\ &= \frac{0.01 \times (3.66 \times 10^{-2})^2}{1} = 1.339 \times 10^{-4} \end{aligned}$$

Problem 7. Calculate the equivalent conductance of acetic acid at infinite dilution at 25°C.

$$\begin{aligned} \text{Given : } \lambda^\circ_{\text{CH}_3\text{COONa}} &= 91.0 \text{ ohm}^{-1} \text{ cm}^2; \quad \lambda^\circ_{\text{NaCl}} = 126.5 \text{ ohm}^{-1} \text{ cm}^2; \\ \lambda^\circ_{\text{HCl}} &= 426.2 \text{ ohm}^{-1} \text{ cm}^2 \end{aligned}$$

$$\begin{aligned} \text{Solution. (a)} \quad \lambda^\circ_{\text{HCl}} &= \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{Cl}^-} = 426.2 \text{ ohm}^{-1} \text{ cm}^2 \\ (b) \quad \lambda^\circ_{\text{NaCl}} &= \lambda^\circ_{\text{Na}^+} + \lambda^\circ_{\text{Cl}^-} = 126.5 \text{ ohm}^{-1} \text{ cm}^2 \\ (c) \quad \lambda^\circ_{\text{CH}_3\text{COONa}} &= \lambda^\circ_{\text{Na}^+} + \lambda^\circ_{\text{CH}_3\text{COO}^-} = 91.0 \text{ ohm}^{-1} \text{ cm}^2 \end{aligned}$$

Adding (a), (c) and subtracting (b), one has

$$\begin{aligned} (a) + (c) - (b) &= \lambda^\circ_{\text{HCl}} + \lambda^\circ_{\text{CH}_3\text{COONa}} - \lambda^\circ_{\text{NaCl}} \\ &= \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{Cl}^-} + \lambda^\circ_{\text{CH}_3\text{COO}^-} + \lambda^\circ_{\text{Na}^+} - \lambda^\circ_{\text{Na}^+} - \lambda^\circ_{\text{Cl}^-} \\ &= \lambda^\circ_{\text{CH}_3\text{COO}^-} + \lambda^\circ_{\text{H}^+} = \lambda^\circ_{\text{CH}_3\text{COOH}} \\ &= 426.2 + 91 - 126.5 \\ \lambda^\circ_{\text{CH}_3\text{COOH}} &= 390.7 \text{ ohm}^{-1} \text{ cm}^2 \end{aligned}$$

Problem 8. The conductivity of an aqueous solution of sodium chloride in a cell is $92 \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance offered by this cell is 247.8 ohm. Calculate the cell constant for this cell. (CBSE Sample Paper 1997)

$$\begin{aligned} \text{Solution. Cell constant} &= \text{Specific conductivity} \times \text{Resistance} \\ &= 92 \text{ ohm}^{-1} \text{ cm}^{-1} \times 247.8 \text{ ohm} = 22797.6 \text{ cm}^{-1} \end{aligned}$$

Problem 9. The resistivity of 0.02 M potassium chloride solution is $361 \text{ } \Omega \text{ cm}$ and a conductivity cell containing such a solution was found to have a resistance of 550 Ω . What is the cell constant?

$$\begin{aligned} \text{Solution. Resistivity} &= \frac{1}{\text{Specific conductivity}} = 361 \text{ } \Omega \text{ cm} \\ \therefore \text{Specific conductivity} &= \frac{1}{361 \text{ } \Omega \text{ cm}} = \frac{1}{361} \text{ S cm}^{-1} \\ \text{Cell constant} &= \text{Specific conductivity} \times \text{Resistance} \\ &= \frac{1 \text{ S cm}^{-1}}{361} \times 550 \text{ } \Omega = 1.52 \text{ cm}^{-1} \end{aligned}$$

Problem 10. The resistance of a conductivity cell filled with 0.01 N solution of NaCl is 200 ohms at 25°C. Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is unity. (CBSE 1992)

$$\text{Solution. Specific conductivity } (\kappa) = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{1 \text{ cm}^{-1}}{200 \text{ ohm}}$$



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$$\text{Volume occupied by the close-packed spheres} = 6 \times \frac{4}{3} \pi r^3$$

$$\text{Volume of the hexagon} = \text{Area of the base} \times \text{Height}$$

$$= 6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \sqrt{\frac{2}{3}}$$

$$\% \text{ of space occupied by spheres} = \frac{\text{Volume occupied}}{\text{Total volume}}$$

$$= \frac{6 \times \frac{4}{3} \pi r^3 \times 100}{6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \sqrt{\frac{2}{3}}} = 74\%$$

$$\% \text{ of empty space} = 100\% - 74\% = 26\%$$

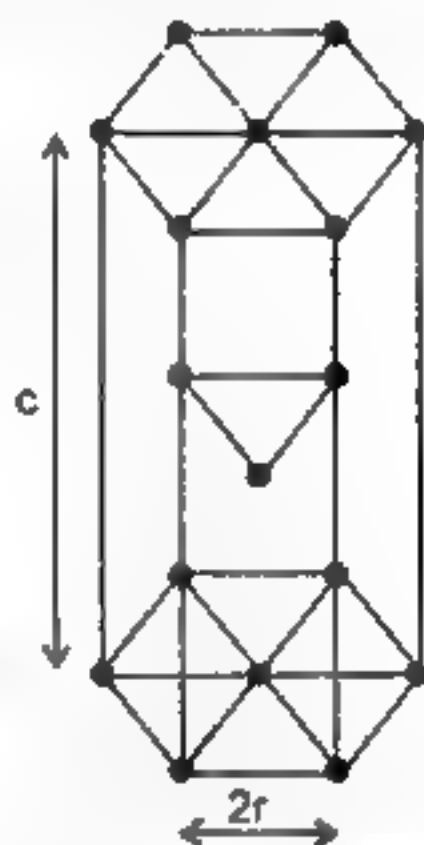


Fig. 42.2 Unit-cell of HCP.

ELEMENTS OF SYMMETRY

1. **Centre of symmetry.** An imaginary point within the crystal, through which a line when extended in opposite directions intersects the opposite faces at equal distances.

2. **Axis of symmetry.** An imaginary line passing through the crystal such that when the crystal is rotated about the line we get an equivalent configuration. A crystal having an n fold axis of symmetry means we get an equivalent configuration after rotation by an angle of $(360/n)$ where $n = 1, 2, 3 \dots$ and so on.

3. **Plane of symmetry.** An imaginary plane passing through the crystal such that it divides the crystal into two equal halves—one half being the mirror image of the other.

4. **Crystallography and its laws.** The science dealing with the study of structural geometry and properties of a crystal is called crystallography.

5. **Law of constancy of Interfacial angles.** The plane surfaces of the crystals are called faces of the crystals. The angles between the faces of crystals are called its interfacial angles. The angles between the faces of crystals of the same substance are always the same which is known as the *law of constancy of interfacial angles*. Crystallization of a saturated solution of a solid in a suitable solvent forms large as well as small crystals of the solid. The sizes of crystals of a substance may be different but the shape and the interfacial angles are always the same.

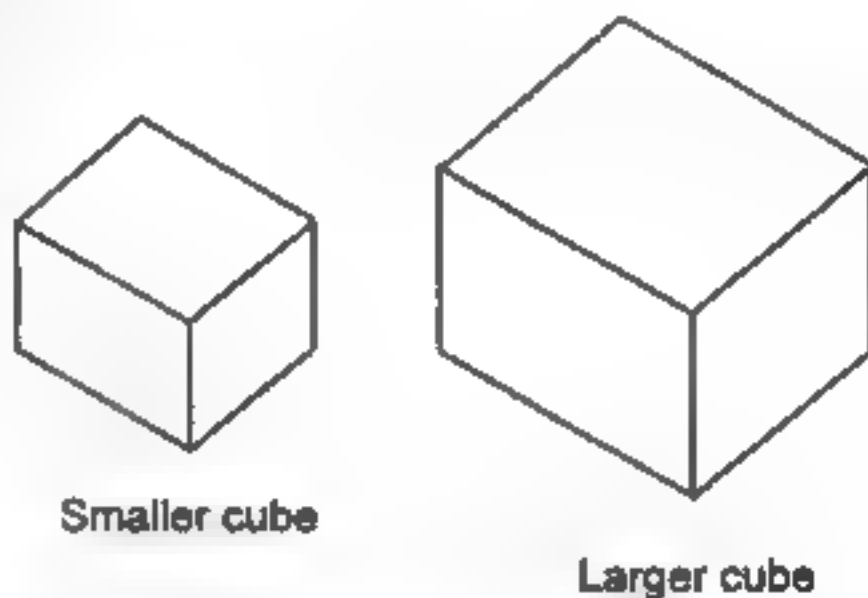


Fig. 42.3 Small and large crystals

6. **The law of symmetry.** All crystals of the same substance possess the same elements of symmetry.

7. **The law of rationality of indices.** The law states that any possible face of a crystal corresponds to a set of indices and the most likely faces are those whose indices are small whole numbers.

A crystal structure can be studied by considering a set of three axis with their origin lying at a lattice point of the crystal. A unit plane makes the intercepts a' , b' , c' on these



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4. If close-packed arrangement is of C atoms, then there can be maximum of $2 \times A$ atoms in the tetrahedral voids and B atoms in the octahedral voids.

✓ SOLVED PROBLEMS

Problem 1. Predict the structure of MgO crystal and co-ordination number of its cation in which cation and anion are equal to 65 pm and 140 pm respectively.

(CBSE 1998)

Solution. Radius ratio, $\frac{r^+}{r^-} = \frac{65 \text{ pm}}{140 \text{ pm}} = 0.464$

Since the radius ratio (0.464) is in between 0.414 and 0.732, MgO has a face-centered cubic lattice (6 : 6 arrangement). The co-ordination number of the cation is 6.

Problem 2. If the radius of the anion in an ionic solid is 100 pm, what should be the radius of the cation: (i) that fits the cubic hole exactly, (ii) that fits the octahedral hole exactly, (iii) that fits the tetrahedral hole exactly.

Solution. (i) $r = 0.73 R = 0.73 \times 100 \text{ pm} = 73 \text{ pm}$;

(ii) $r = 0.414 R = 0.414 \times 100 \text{ pm} = 41.4 \text{ pm}$

(iii) $r = 0.225 R = 0.225 \times 100 \text{ pm} = 22.5 \text{ pm}$.

Problem 3. Predict the close-packed structure of an ionic compound A^+B^- in which the radius of cation = 148 pm and radius of anion = 195 pm. What is the coordination number of cation?

(CBSE 1998)

Solution. Radius ratio, $\frac{r^+}{r^-} = \frac{148 \text{ pm}}{195 \text{ pm}} = 0.759$

As the value of radius ratio (0.759) is more than (0.732), the crystalline solid A^+B^- has body-centered cubic lattice. The co-ordination number of $A^+ : B^- :: 8 : 8$.

Problem 4. A solid A^+B^- has NaCl type close-packed structure. If the anion has a radius of 241.5 pm, what should be the minimum radius of the cation? Can a cation, C^+ having radius of 50 pm be fitted into the tetrahedral hole of the crystal A^+B^- ?

(CBSE 1998)

Solution. Limiting radius ratio for an octahedral hole

$$= \frac{\text{Size of the cation } A^+}{\text{Size of the anion } B^-} = \frac{r^+}{r^-} = 0.414$$

$$r^+ = 0.414 r^- = 0.414 \times 241.5 \text{ pm} = 99.98 \text{ pm}.$$

For a tetrahedral hole $= \frac{r^+}{r^-} = 0.225$

The minimum radius of the cation A^+ to fit exactly into the octahedral hole should be 99.98 pm.

$$r^+ = 0.225 r^- = 0.225 \times 241.5 \text{ pm} = 54.34 \text{ pm}.$$

Since the size of the cation C^+ (50 pm) is less than the ideal radius (54.34 pm), it can be fitted into tetrahedral hole of the crystal A^+B^- .

Problem 5. A solid A^+B^- has NaCl type closed packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation? Can a cation C^+



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$$\begin{aligned}
 \text{or} \quad \text{Atomic mass} &= \frac{\text{Density} \times \text{Unit-cell volume (cm)}^3 \times N_{\text{Avo}}}{Z} \\
 &= \frac{19.35 \text{ g cm}^{-3} \times 3.2 \times 10^{-23} \text{ cm}^3/\text{unit-cell} \times 6.023 \times 10^{23} \text{ atoms/mol}}{2 \text{ atoms/unit-cell}} \\
 &= 186.5 \text{ g/mol}
 \end{aligned}$$

186.5 g of the element contains N_{Avo} atoms = 6.023×10^{23} atoms

$$\begin{aligned}
 50 \text{ g of the element contains } N_{\text{Avo}} \text{ atoms} &= 6.023 \times 10^{23} \text{ atoms} \times \frac{50 \text{ g}}{186.5 \text{ g}} \\
 &= 1.614 \times 10^{23} \text{ atoms}
 \end{aligned}$$

Problem 8. An element of atomic mass 98.5 g mol^{-1} occurs in FCC structure. If its unit-cell edge length is 500 pm and its density is 5.22 g cm^{-3} , what is the value of Avogadro constant? (CBSE 1997)

Solution. Unit-cell edge length, $a = 500 \text{ pm} = 500 \text{ pm} \times \frac{1 \text{ cm}}{10^{10} \text{ pm}} = 500 \times 10^{-10} \text{ cm}$

$$\text{Unit-cell volume, } a^3 = (500 \times 10^{-10} \text{ cm})^3 = 125 \times 10^{-24} \text{ cm}^3$$

$$\text{Density} = \frac{\text{Atomic mass} \times Z}{\text{Unit-cell volume (cm)}^3 \times \text{Avogadro number}}$$

$$\begin{aligned}
 \text{or} \quad \text{Avogadro number} &= \frac{\text{Atomic mass} \times Z}{\text{Unit-cell volume (cm)}^3 \times \text{Density}} \\
 &= \frac{98.5 \text{ g mol}^{-1} \times 4}{125 \times 10^{-24} \text{ cm}^3 \times 5.22 \text{ g cm}^{-3}} \\
 &= 6.03 \times 10^{23} \text{ mol}^{-1}
 \end{aligned}$$

Problem 9. Given for Fe: $a \text{ pm} = 286$, $\rho \text{ g cm}^{-3} = 7.86$. Find the type of cubic lattice to which the crystal belongs. Also calculate the radius of iron. (At. Wt. of Fe = 55.85) (CBSE 1992 Compt.)

Solution. Length of edge of the unit-cell = 286 pm

$$= 286 \text{ pm} \times \frac{1 \text{ cm}}{10^{10} \text{ pm}} = 286 \times 10^{-10} \text{ cm}$$

$$\text{Volume of the unit-cell} = (286 \times 10^{-10} \text{ cm})^3 = 2.34 \times 10^{-23} \text{ cm}^3$$

$$\begin{aligned}
 Z &= \frac{\text{Unitcell volume (cm)}^3 \times \text{Density} \times N_{\text{Avo}}}{\text{Molar mass of Fe}} \\
 &= \frac{2.34 \times 10^{-23} \text{ cm}^3 \times 7.86 \text{ g/cm}^3 \times 6.023 \times 10^{23} \text{ atoms/mol}}{55.85 \text{ g/mol}} = 2.
 \end{aligned}$$

As the number of atoms per unit-cell is 2, iron has body-centered cubic crystal structure.

$$a = \frac{2}{\sqrt{3}} \cdot d = \frac{2}{\sqrt{3}} (2r)$$

$$r = \frac{\sqrt{3}}{4} \times a = \frac{\sqrt{3}}{4} \times 286 \text{ pm} = 123.8 \text{ pm}$$



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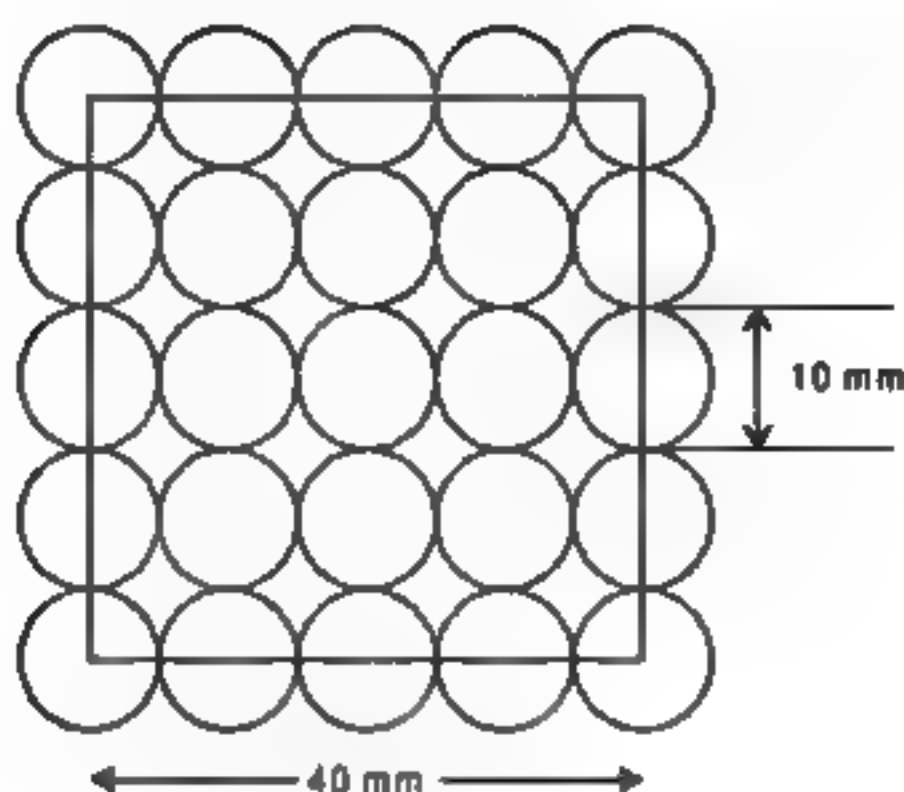


Fig. 44.2

Number of marbles per unit area

$$\begin{aligned}
 &= \frac{25 \text{ marbles}}{(40 \text{ mm})^2} = \frac{25}{(4 \text{ cm})^2} \\
 &= 1.5625 \text{ marbles/cm}^2
 \end{aligned}$$

Problem 27. (i) AB crystallizes in a rock salt structure with $A : B = 1 : 1$. The shortest distance between A and B is $y^{1/3}$ nm. The formula mass of AB is $6.023 Y$ amu where Y is any arbitrary constant. Find the density in kg m^{-3} .

(ii) If measured density is 20 kg m^{-3} . Identify the type of point defect.

(IIT Mains 2004)

Solution. (i) Rock-salt has FCC structure : $Z = 4$

$$\begin{aligned}
 \text{Edge-length of FCC unit cell} &= 2 \times \text{Shortest distance between } A^+ \text{ and } B^- \\
 &= 2 \times y^{1/3} \text{ nm} = 2 \times y^{1/3} \times 10^{-9} \text{ m}
 \end{aligned}$$

$$\begin{aligned}
 \text{Density of the crystal} &= \frac{Z \times M}{N_{\text{Avo}} \times a^3} \\
 &= \frac{4 \times 6.023 Y}{6.023 \times 10^{23} \times (2 \times y^{1/3} \text{ cm} \times 10^{-9} \text{ m})^3} \\
 &= 5 \times 10^3 \text{ g/m}^3 = 5 \text{ kg/m}^3
 \end{aligned}$$

(ii) As there is huge difference in theoretically calculated density and actual density, the given solid has metal excess defect or interstitial defect.



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1. Gas analysis or Eudiometry. It is a technique of determining the *percentage-composition by volume* of gaseous mixtures, molecular formulae of gases and gaseous hydrocarbons. The gas analysis is carried out in a graduated tube called an eudiometer.

2. Eudiometer. It is a graduated glass tube with platinum electrodes, closed at one end, used to measure volume changes during combination of gases.

Combustion methods :

- A known volume of the gaseous hydrocarbon is mixed with a known excess of oxygen and the mixture so obtained is exploded electrically in the eudiometer tube.
- The carbon and hydrogen of the gaseous mixture are oxidized to carbon dioxide and water respectively.

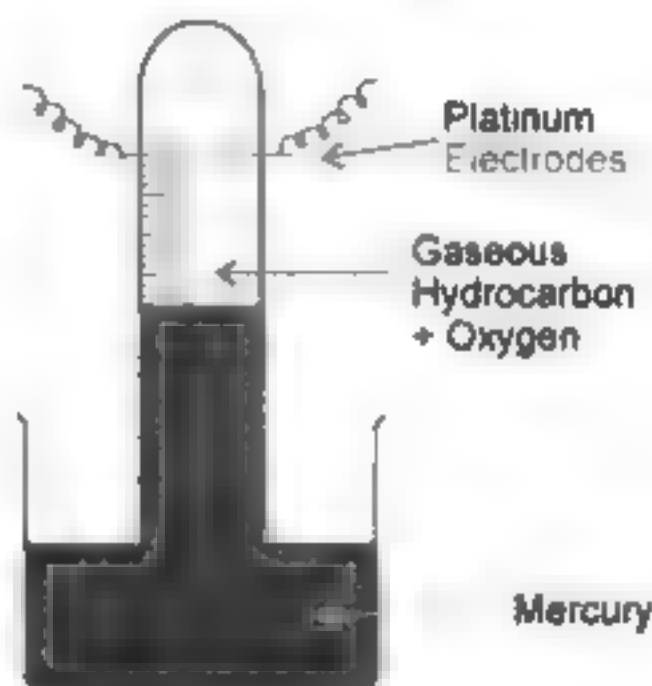


Fig. 45.1 Measurement of volume changes during combination of gases.



- Measurement of change in volume during combination of gases.** The whole apparatus is allowed to cool down to room temperature. Let the measured volume of the gaseous mixture after combustion be V_2 . This volume corresponds to the volume of CO_2 and unused O_2 . *Water formed during combustion becomes a liquid at room temperature and so occupies negligible volume.* There is usually contraction in volume in combustion of hydrocarbons.
- Measurement of volume of residual unused oxygen.** When a little alkali (NaOH or KOH) is introduced into the eudiometer, CO_2 is absorbed by it. There is further contraction in volume and now the measured volume is the volume of unused oxygen (V_3).

$$\therefore \text{Volume of } CO_2 \text{ formed during combustion} = V_3 - V_2$$

It should be noted that all measurements of volumes are done under identical conditions, *i.e.*, at the same temperature and pressure.

3. Absorption methods. If the gaseous mixture contains several gases, the volumes occupied by each of the gas is determined by treating the mixture with a series of *absorbents* at the same temperature and pressure.



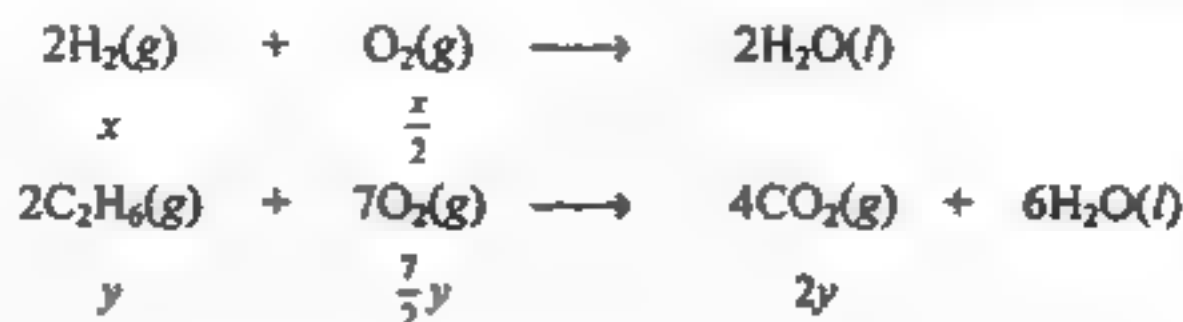
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$$\text{Contraction due to combustion of H}_2 = x + \frac{x}{2} = \frac{3}{2}x$$

$$\text{Contraction due to combustion of ethane} = y + \frac{7}{2}y - 2y = \frac{5}{2}y$$

$$\text{Total contraction in volume} = \frac{3}{2}x + \frac{5}{2}y$$

$$\text{Contraction in volume} + \text{CO}_2 \text{ produced} = (15 + 100) - 86.5 = 28.5 \text{ mL}$$

$$\therefore \frac{3}{2}x + \frac{5}{2}y + 2y = 81 \quad \dots(i)$$

As air contains 21% by volume of oxygen,

$$\text{Volume of O}_2 \text{ taken} = 100 \times \frac{21}{100} = 21 \text{ mL}$$

$$\text{Volume of unused O}_2 = 86.5 - 81 = 5.5 \text{ mL}$$

$$\text{Volume of O}_2 \text{ consumed} = 21 - 5.5 = 15.5 \text{ mL}$$

$$\therefore \text{Volume of O}_2 \text{ consumed in the combustion of H}_2 = \frac{x}{2}$$

$$\text{Volume of O}_2 \text{ consumed in the combustion of ethane} = \frac{7}{2}y$$

$$\begin{aligned}
 \therefore \quad \frac{x}{2} + \frac{7}{2}y &= 15.5 & \dots(ii) \\
 \frac{x}{2} &= 15.5 - \frac{7}{2}y
 \end{aligned}$$

Substitute the value of $\frac{x}{2}$ in eq. (i),

$$3\left(15.5 - \frac{7}{2}y\right) + \frac{5}{2}y + 2y = 81$$

$$93 - 21y + 5y + 4y = 81$$

$$12y = 36$$

$$y = 3 \text{ mL}$$

$$\frac{x}{2} = 15.5 - \frac{7}{2} \times 3 = \frac{10}{2}$$

$$x = 10 \text{ mL}$$

$$z = 15 - (10 + 3) = 2 \text{ mL}$$

$$\text{Percentage volume H}_2 = \frac{10 \text{ mL}}{15 \text{ mL}} \times 100 = 66.67\%$$



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Given : Volume of O_2 used = 30 mL

$$\therefore 10 \left(x + \frac{y}{4} \right) = 30 \quad \dots(i)$$

Volume of CO_2 formed = 20 mL

$$10x = 20 \quad \text{or } x = 2$$

Substituting the value of $x = 2$ into eq. (i), one has

$$x + \frac{y}{4} = 3$$

$$2 + \frac{y}{4} = 3 \quad \text{or } y = 4$$

\therefore Molecular formula of the hydrocarbon is C_2H_4 .

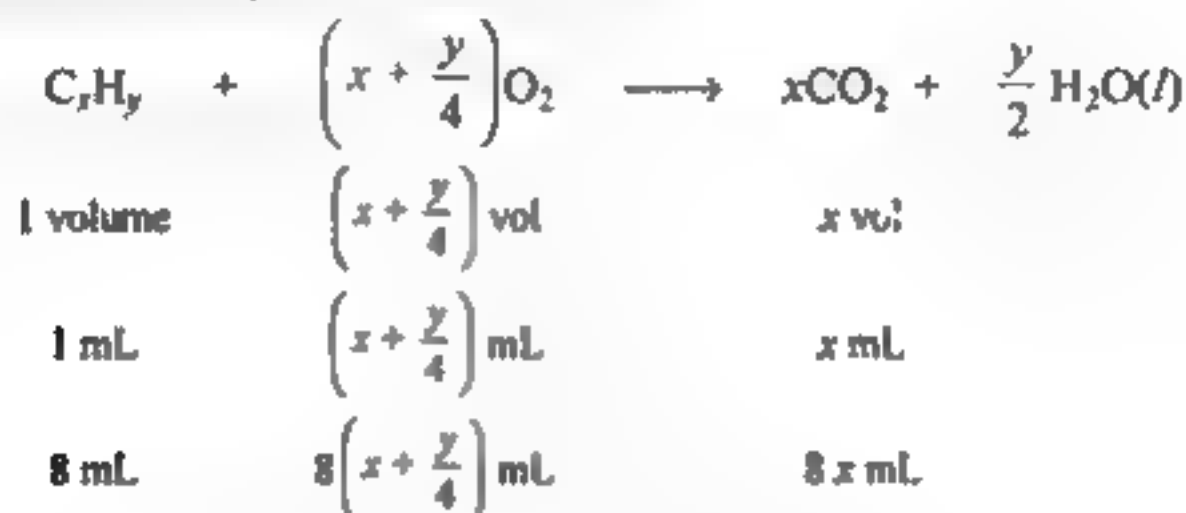
Problem 16. 8 mL of a gaseous hydrocarbon was mixed with excess of air containing 21% by volume of oxygen and exploded in a eudiometer tube. After cooling the contraction in volume was measured to be 28 mL. This residual gas when treated with KOH solution contracted by 32 mL. Determine the molecular formula of the hydrocarbon. All volumes are measured at the same temperature and pressure.

Solution. Volume of gaseous hydrocarbon = 8 mL

Contraction after combustion and cooling = 28 mL

Volume of CO_2 formed = 32 mL

Let the formula of the hydrocarbon be C_xH_y .



$$\text{Contraction in volume} = 8 + 8 \left(x + \frac{y}{4} \right) - 8x$$

$$\text{Given :} \quad 28 = 8 + 8 \frac{y}{4}$$

$$\text{or} \quad y = 10$$

$$\text{Volume of } CO_2 \text{ formed} = 8x = 32$$

$$x = 4$$

The Molecular formula of the hydrocarbon is C_4H_{10} .

Problem 17. Ten millilitre of a gaseous organic compound containing C, H and O only was mixed with 100 mL of oxygen and exploded under conditions which allowed the water formed to condense. The volume of the gas after explosion was 90 millilitre. On treatment with potash solution a further contraction in volume of 20 millilitre was observed. Given that the vapour density of the compound is 23, deduce the molecular formula. All volume measurements are carried out under the same conditions of temperature and pressure.



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Analysis of Organic Compounds

ESTIMATION OF ELEMENTS

1. ANALYSIS OF ORGANIC COMPOUNDS

Various sophisticated techniques like differential extraction and chromatography are employed to purify an organic compound before proceeding for its characterization. The next steps for determining its molecular structure are detection of extra-elements, estimation of elements, determination of molecular mass, calculation of molecular formula and finally identification of functional groups by physical methods or chemical tests.

2. ESTIMATION OF CARBON AND HYDROGEN IN AN ORGANIC COMPOUND

A known mass of the given organic compound is heated with excess of dry oxygen in presence of cupric oxide. Carbon is oxidized to carbon dioxide gas and hydrogen is oxidized to water vapour. The vapours evolved are then passed into an already weighed U-tube containing anhydrous calcium chloride where water vapour is absorbed. The remaining carbon dioxide gas is then absorbed by passing it through a strong solution of potassium hydroxide or ascarite ($\text{NaOH} + \text{CaO}$).



At the end of the experiment, the U-tubes are weighed again and by subtraction of initial masses, the amount of water and CO_2 formed are calculated.

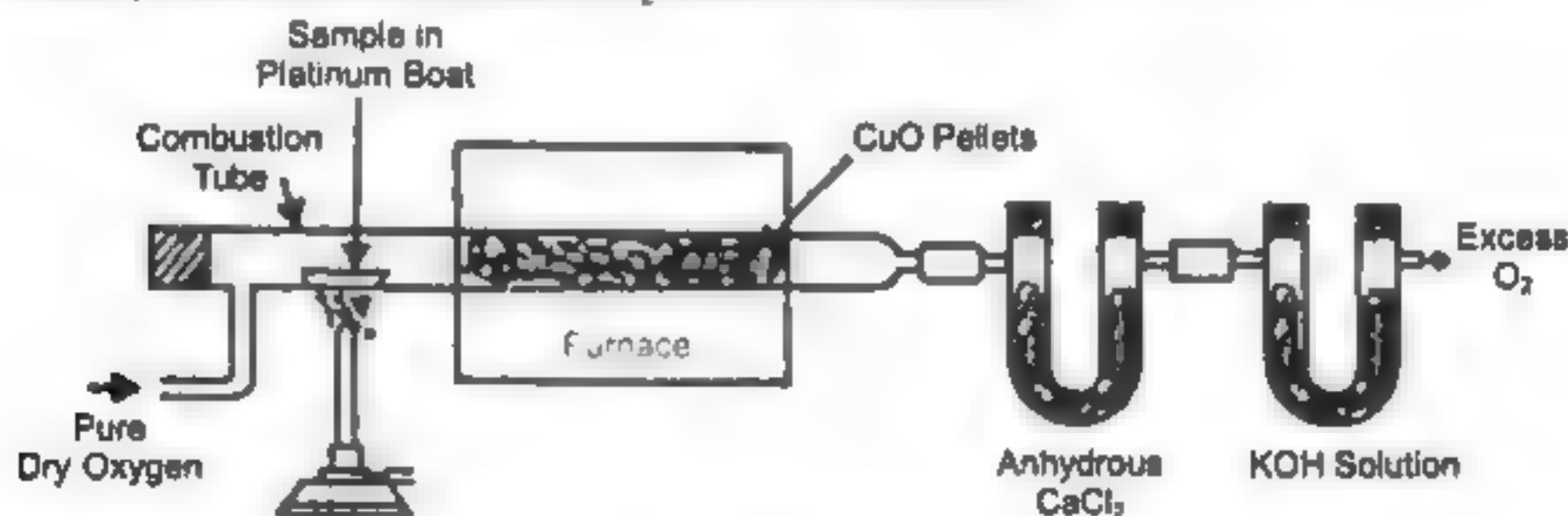


Fig. 46.1 Apparatus for estimation of carbon and hydrogen.

Calculations :

- Mass of the organic compound = W g
- Initial mass of U-tube containing CaCl_2 = x_1 g
- Final mass of U-tube containing CaCl_2 = x_2 g
- Mass of water vapour evolved = $x_2 - x_1 = W_1$ g



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Volume of 0.1 N Na_2CO_3 used for neutralizing excess acid,

$$V_2 = 40 \text{ mL}$$

Volume of 0.1 N H_2SO_4 used for neutralizing NH_3 gas 110 mL of 0.1 N H_2SO_4

$$= 150 \text{ mL} - 40 \text{ mL} = 110 \text{ mL}$$

$$= 110 \text{ mL of } 0.1 \text{ N } \text{NH}_3$$

$$= 110 \text{ mL of } 0.1 \text{ N Nitrogen}$$

$$= \left(\frac{110}{1000} \right) \text{ litre} \times 0.1 \text{ N} \times 14 \text{ g N}$$

$$\text{Percentage of nitrogen} = \frac{14 \times N \times (V \text{ mL})}{1000} \times \frac{100}{W \text{ g}} \%$$

$$= \frac{14 \times 0.1 \text{ N} \times (110 \text{ mL})}{1000} \times \frac{100}{0.4965 \text{ g}} = 31\% \text{ N.}$$

(B) DUMA'S METHOD

A weighed amount of the given organic compound is heated strongly with cupric oxide in a current of dry carbon dioxide. Carbon and hydrogen are converted into carbon dioxide and water; and nitrogen in the compound is converted into free nitrogen gas. Some of the oxides of nitrogen may also form during the reaction. They are reduced back to nitrogen by passing the evolved gases over a heated copper gauze. The mixture of gases is then passed through a strong solution of potassium hydroxide when all the gases except nitrogen are absorbed. Then the volume of nitrogen gas is measured experimentally at room temperature.

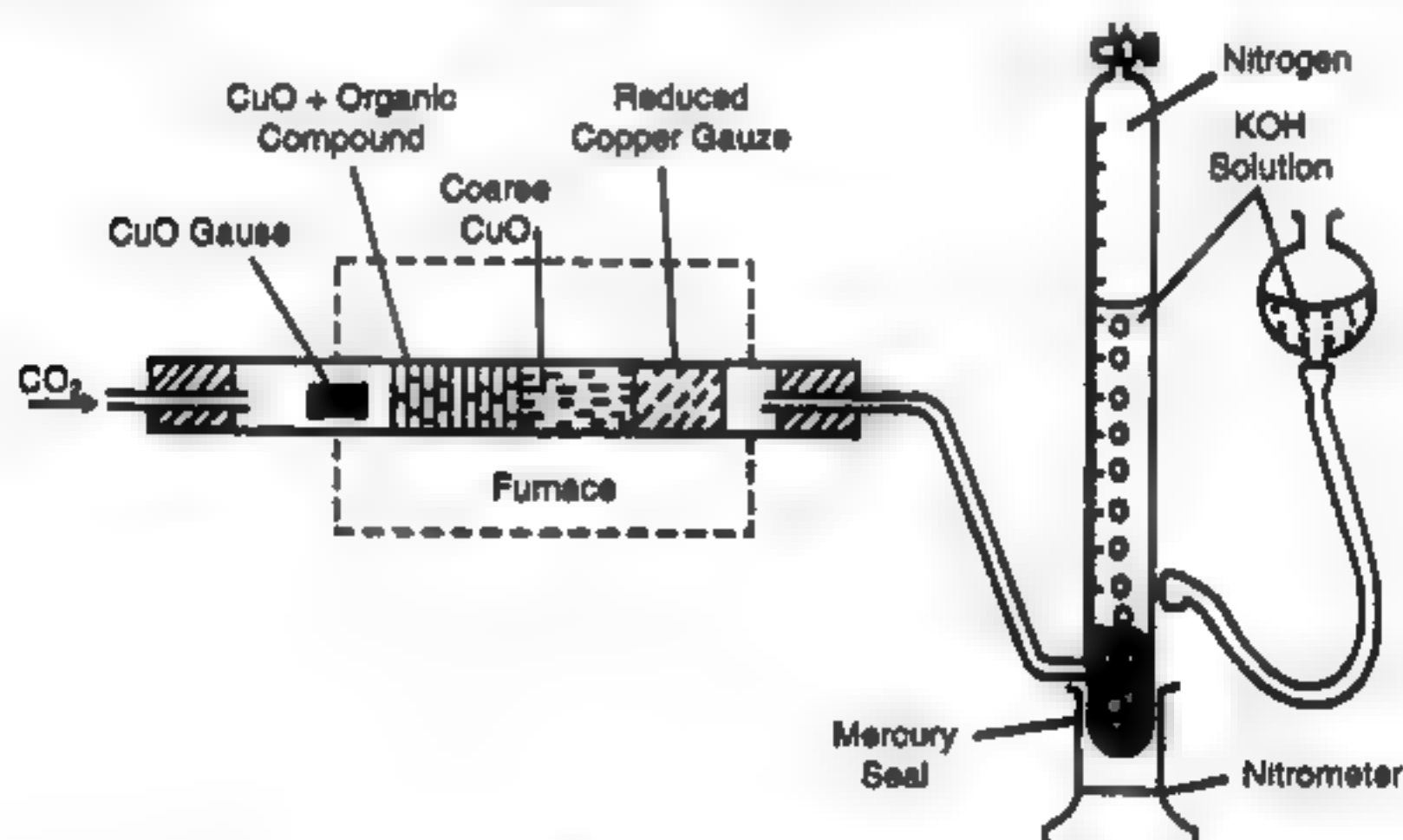


Fig. 48.3 Estimation of nitrogen by Duma's method.

Calculations :

$$\text{Mass of the organic compound} = W \text{ g}$$

$$\text{Volume of } \text{N}_2 \text{ collected at room temperature (} ^\circ\text{C)} = V_1 \text{ mL}$$

$$\text{Atmospheric pressure} = P_1 \text{ mm Hg}$$

$$\text{Volume of nitrogen at STP} = V \text{ mL}$$



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Determination of Molecular Mass and Calculation of Molecular Formula of an Organic Compound

1. DETERMINATION OF MOLECULAR MASS

The molecular mass of a compound can be determined by various methods such as depression in freezing point, elevation of boiling point, measurement of osmotic pressure and lowering of vapour pressure of a solution. These methods have been discussed in detail in the 'Solutions' chapter. The calculation of molecular formula from the percentage of elements in the compound when its molecular mass is given has been discussed in Chapter 2.

Now we shall discuss other methods of determining molecular mass of compounds, *e.g.*, Victor-Meyer's method, silver salt method, the chloroplatinic acid method and volumetric method.

2. VICTOR-MEYER'S METHOD

This method of determining molecular mass is suitable for volatile substances. The determination is carried out using Victor-Meyer's apparatus. A weighed amount of the

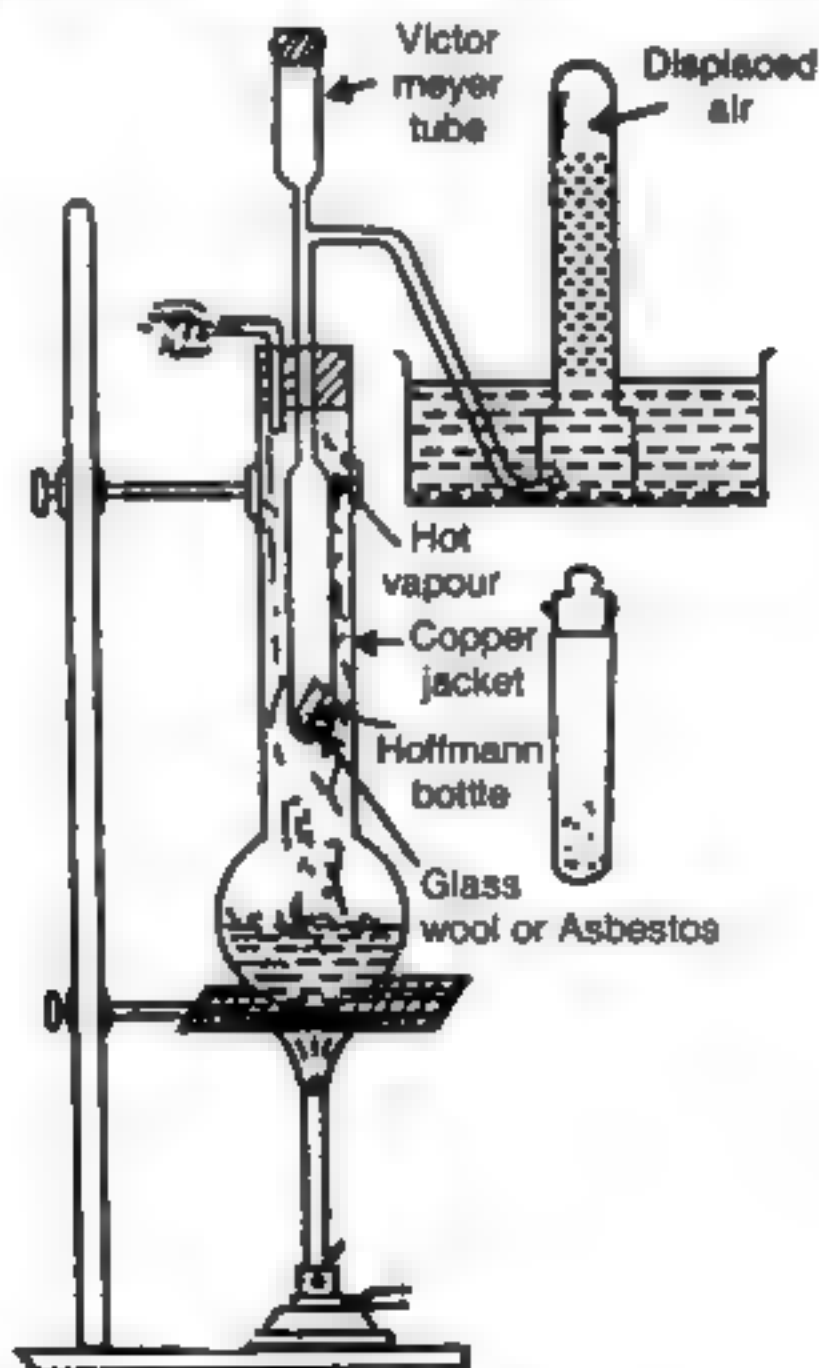


Fig. 47.1 Victor-Meyer's apparatus.



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PROBLEMS FOR PRACTICE

1. In the determination of molecular mass by Victor-Meyer method, 0.35 g of a volatile compound expelled 74.9 mL of air measured over water at 27°C and 758.7 torr. Find the molecular mass of the substance. Aqueous tension of water at 27°C is 26.7 torr.
2. A dibasic aliphatic acid contains 40.7% C, 5.1% H and the rest oxygen. 1.66 g of the silver salt of the acid was ignited when 1.08 g silver residue was obtained. Determine the molecular formula of the acid. Suggest its most probable structure of acid.
3. 0.531 g of silver salt of a tribasic acid was ignited when a residue of 0.324 g of metallic silver was left. Calculate the molecular mass of the acid.
4. The platinichloride of a diacid base contains 42% of platinum. The molecular mass of chloroplatinic acid is 410 g/mol. What is the molecular mass of the diacid base?
5. 0.23 g of a monobasic organic acid was dissolved in 100 mL solution. 10 mL of this solution required 7.5 mL of N/15 NaOH solution for titration to the end point using phenolphthalein indicator. Determine the molecular mass of the acid.
6. 0.1467 g of a tribasic acid required 45 mL of N/20 NaOH solution for complete neutralization. Find the molecular mass of the acid.
7. 0.108 g of an aromatic diacid base required 48 mL of 0.021 M H_2SO_4 for complete neutralization. Calculate the molecular mass of the diacid base.
8. An organic compound contains 39.2% C, 9.8% H, 33.7% P. Calculate its empirical formula.
9. An organic compound contains 28.2% C, 1.57% H, 12.5% S, 13.9% Cl, 31.2% Br and rest oxygen. Calculate its empirical formula.
10. An organic liquid contains 12.8% C, 2.1% H, and 85.1% Br. 0.188 g of it in a Victor Meyer experiment displaced 24.2 mL of moist air measured at 14°C and 752 mm pressure. Find the molecular formula of the substance. Aqueous tension at 14°C is 12 mm.
11. Determine the molecular formula of a dicarboxylic acid from the following data : 0.4 g of the acid gave 0.39 g of CO_2 and 0.08 g of water. 1.0 g of the silver salt of the acid left 0.71 g of silver as residue on ignition.
12. 0.2070 g of a monoacid organic base on combustion yielded 0.3756 g CO_2 and 0.0960 g water. 0.1122 g of the substance gave 28.55 mL N_2 at 20°C and 757.4 mm Hg. The aqueous tension at 20°C is 17.4 mm Hg. The platinochloride of the salt of the base yielded 32.28% metallic platinum on ignition. Calculate the molecular formula of the base.
13. An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.05 M sulphuric acid. The excess acid required 25 mL of 0.1 M sodium hydroxide for neutralization. Determine the molecular formula of the compound if its molecular weight is 121. Draw two possible structures for this compound.
14. An aromatic dibasic acid contains 45.5% carbon, 2.37% hydrogen and 6.64% nitrogen. 0.192 g of this acid is treated with 50 mL of 0.093 N caustic soda. The



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(iii) In the Cannizzaro reaction given below,

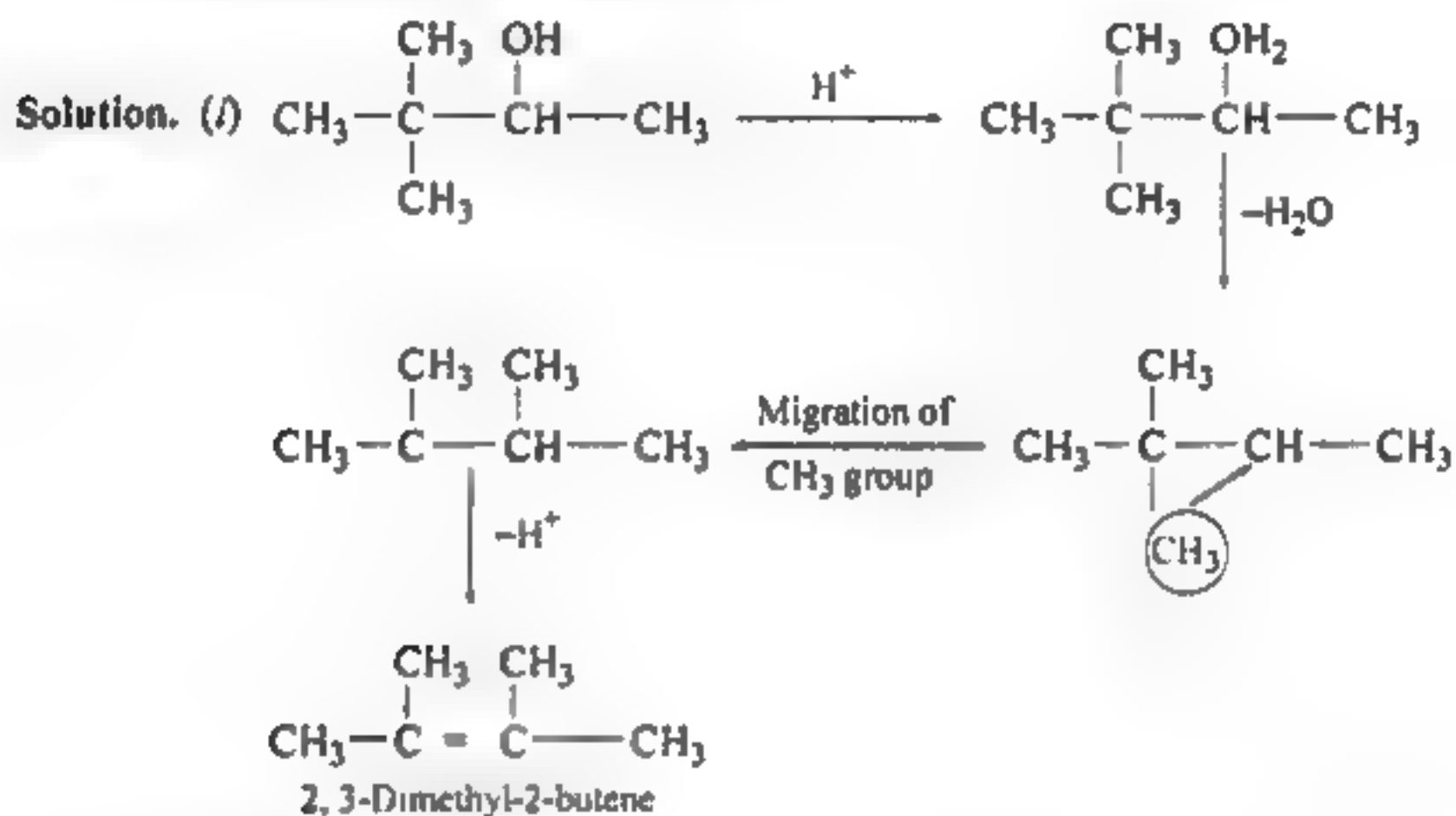


the slowest step is

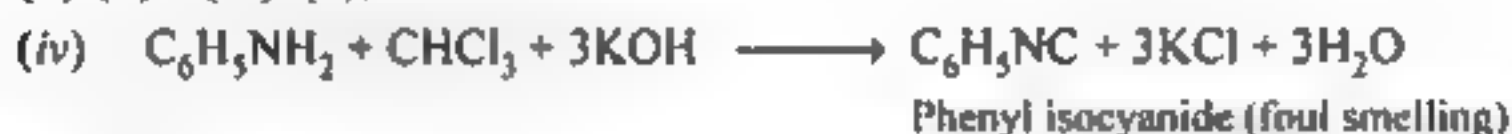
[IIT/JEE 96]

- the attack of ^-OH at the carbonyl group,
- the transfer of hydride to the carbonyl group,
- the abstraction of proton from the carboxylic acid,
- the deprotonation of $\text{Ph}-\text{CH}_2\text{OH}$.

(iv) Write the structure of the foul-smelling compound obtained when aniline is treated with chloroform in the presence of KOH.



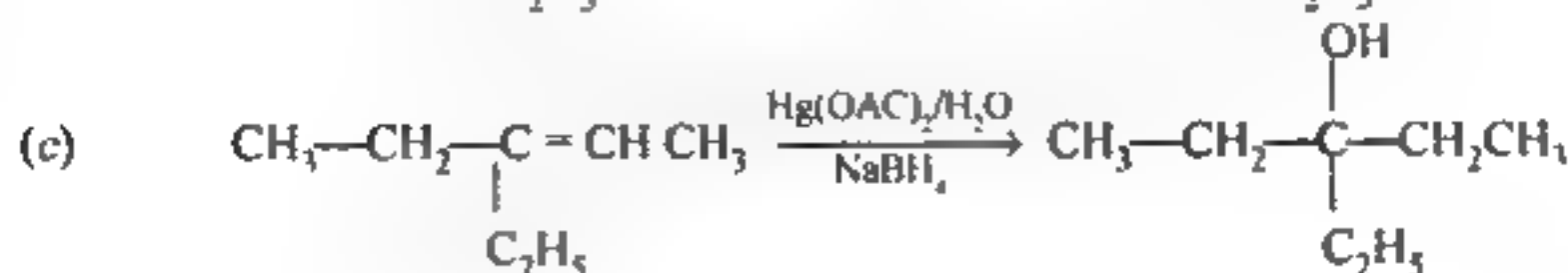
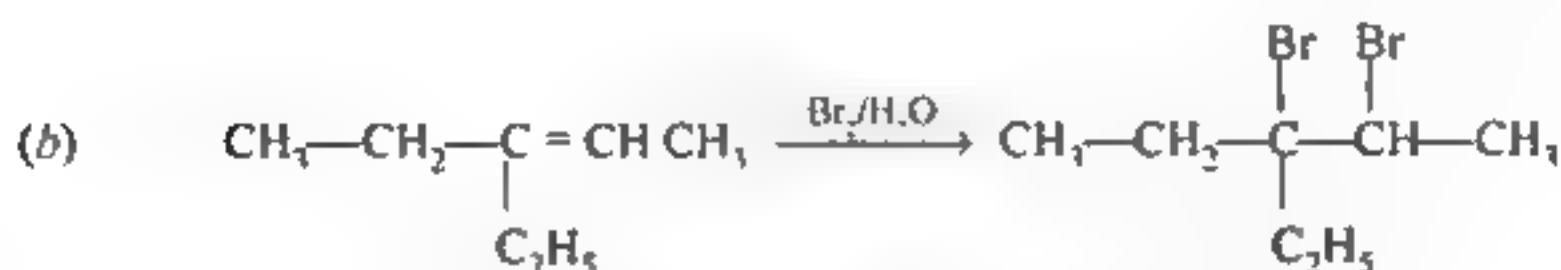
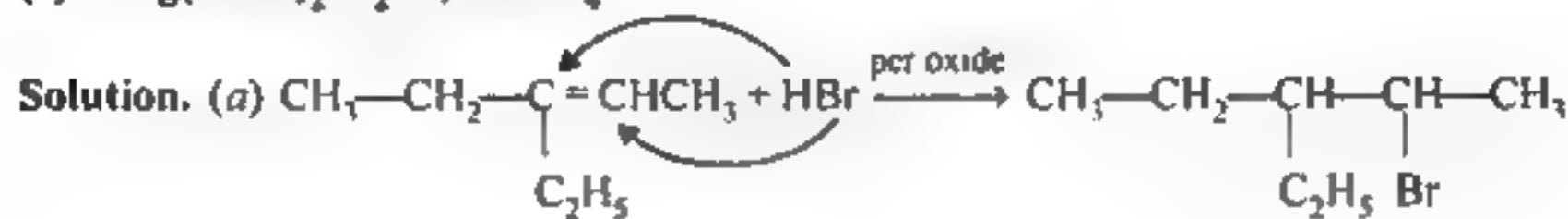
(ii) (d) (iii) (b).



Problem 7. Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions. [IIT/JEE 96]

(a) HBr in the presence of peroxide (b) $\text{Br}_2/\text{H}_2\text{O}$

(c) $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$; NaBH_4





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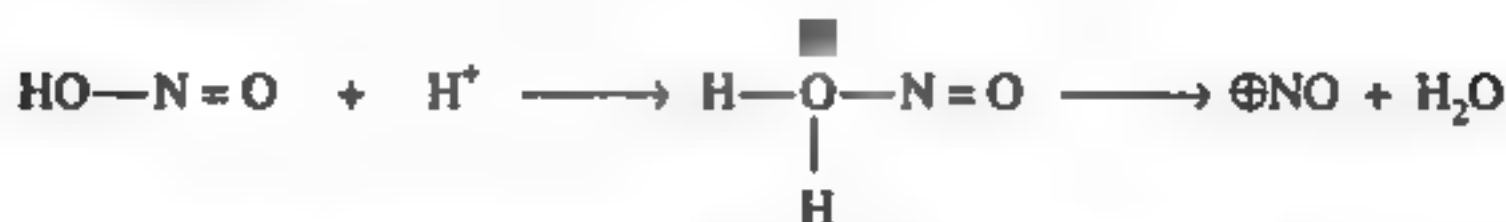
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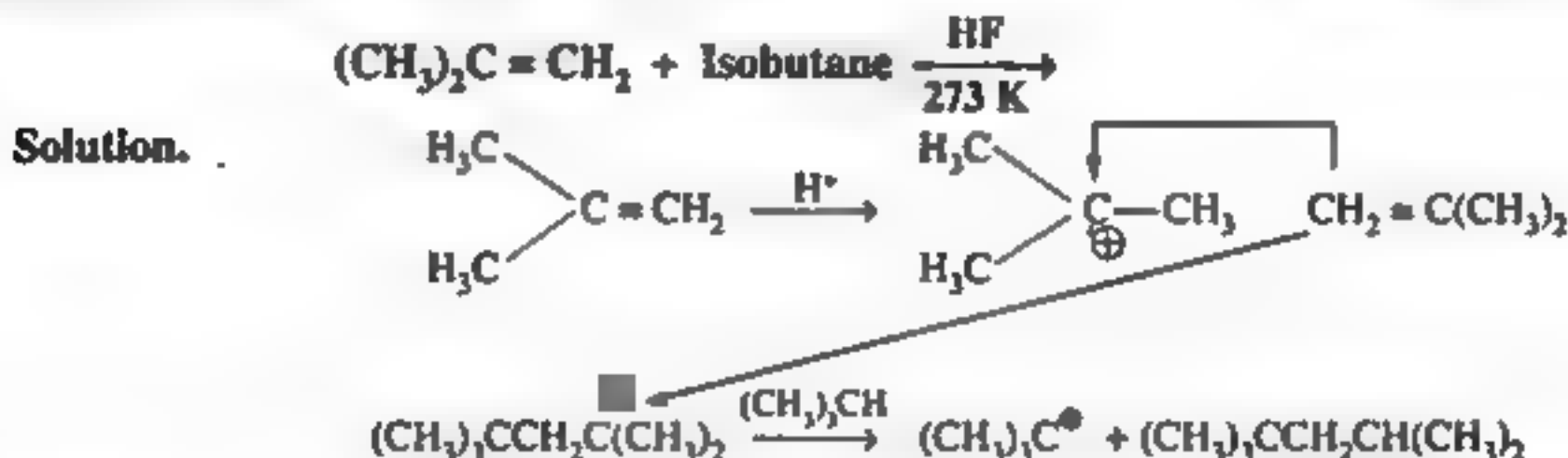
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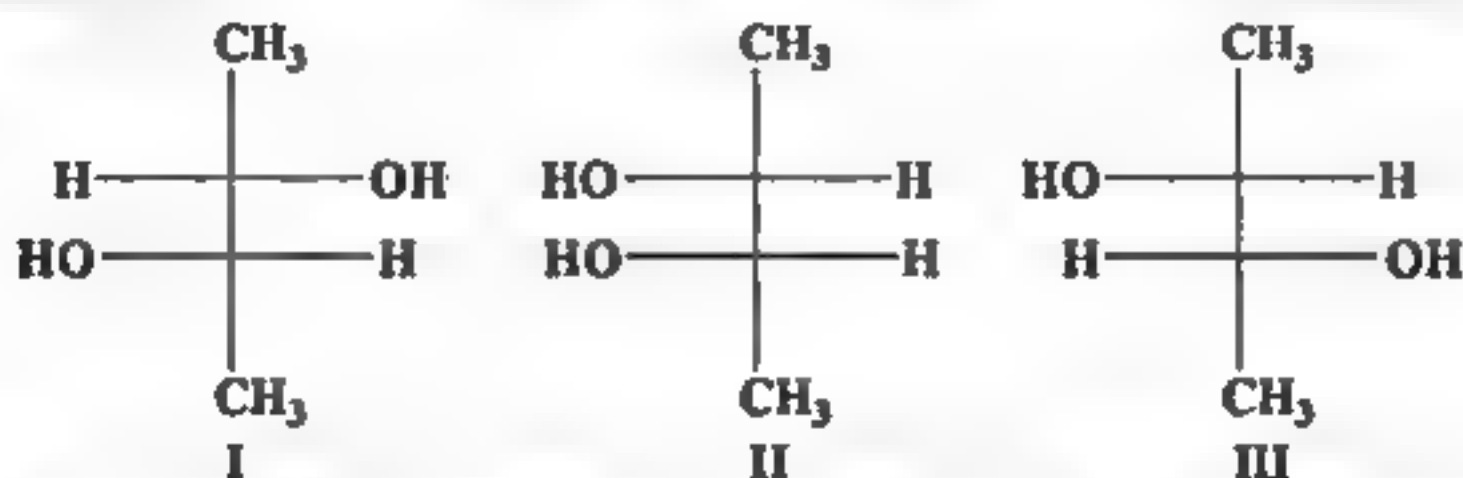
Mineral acid is used for formation of HNO_2 , as well as it acts as an acid.

Problem 38. Complete the reaction :

[Roorkee 1999]



Problem 39. Identify the pairs of enantiomers and diastereomers from the following compounds, I, II and III. [IIT/JEE 2000]



Solution. (I) and (III) are enantiomers. (I) and (II), (II) and (III) are diastereomers.

Problem 40. Give reasons for the following :

[IIT/JEE 2000]

- (i) tert-Butylbenzene does not give benzoic acid on treatment with acidic KMnO_4 .
- (ii) $\text{CH}_2=\text{CH}^-$ is more basic than $\text{HC}\equiv\text{C}^-$.
- (iii) Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds.

Solution. (i) tert-Butylbenzene does not have benzylic hydrogen for oxidation to convert it into benzoic acid.

(ii) Higher the s-character, stronger is the acid. $(\text{CH}\equiv\text{C}^-)$ is conjugate base of stronger acid $(\text{HC}\equiv\text{CH})$ as C has higher percentage of 's' character. So, $\text{HC}\equiv\text{C}^-$ is less basic than $\text{CH}_2=\text{CH}^-$.

(iii) Because the planar benzene nucleus has higher π -electron density. Also in electrophilic addition reaction, benzene loses its aromaticity. Therefore, it undergoes electrophilic substitution reaction in which aromaticity is retained.



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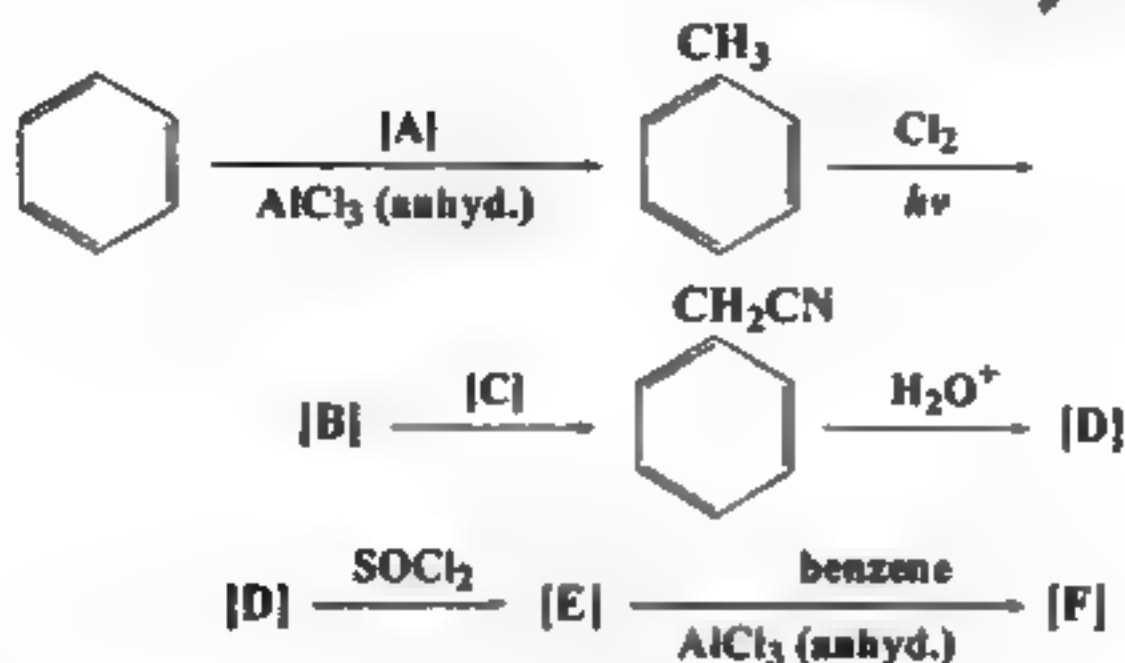
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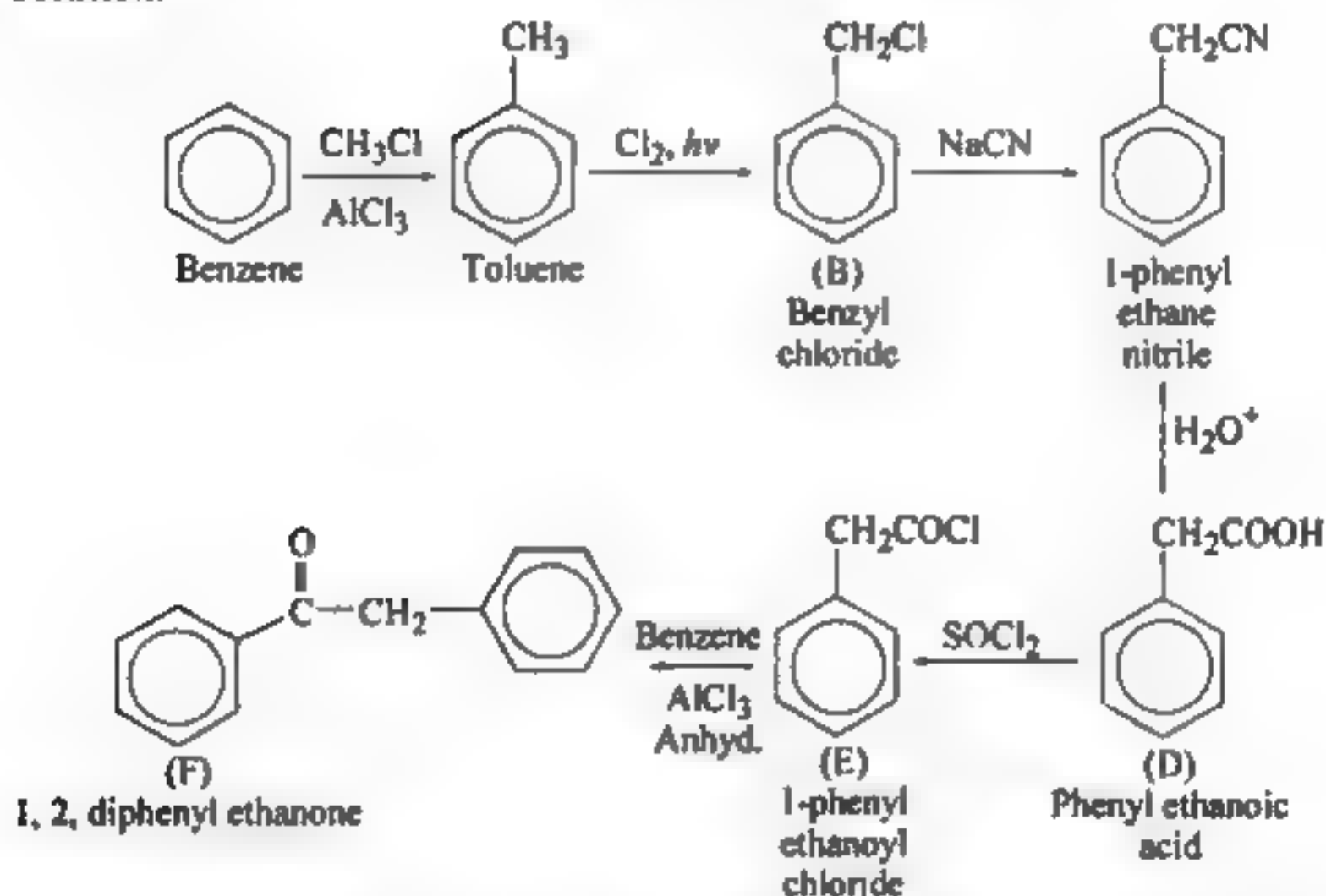
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Solution.



Problem 34. An organic compound (A) has 76.6% C and 6.38% H. Its vapour density is 47. It gives characteristic colour with aq. FeCl_3 solution. (A) when treated with CO_2 and NaOH at 140°C under pressure gives (B) which on being acidified gives (C). (C) reacts with acetyl chloride to give (D) which is a well-known pain killer. Identify (A), (B), (C) and (D) and explain the reactions involved.

Solution. Vapour density of A = 47

Molecular mass of A = $2 \times \text{V.D.} = 2 \times 47 = 94 \text{ g/mol}$

Calculation of empirical formula :

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|--------------------------------|-------------|---------------------------|----------------------------|--------------|
| C | 76.60 | 12 | $\frac{76.60}{12} = 6.38$ | $\frac{6.38}{1.06} = 6.01$ | 6 |
| H | 6.38 | 1 | $\frac{6.38}{1} = 6.38$ | $\frac{6.38}{1.06} = 6.01$ | 6 |
| O | $100 - (76.60 + 6.38) = 17.02$ | 16 | $\frac{17.02}{16} = 1.06$ | $\frac{1.06}{1.06} = 1$ | 1 |



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Calculation of empirical formula :

| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|---------------------------|--------------------------|--------------|
| C | 26.66 | 12 | $\frac{26.66}{12} = 2.22$ | $\frac{2.22}{2.22} = 1$ | 1 |
| H | 2.22 | 1 | $\frac{2.22}{1} = 2.22$ | $\frac{2.22}{2.22} = 1$ | 1 |
| O | 71.12 | 16 | $\frac{71.12}{16} = 4.45$ | $\frac{4.45}{2.22} = 2$ | 2 |

∴ The empirical formula is CHO_2 .

Empirical formula mass = $12 + 1 + 2 \times 16 = 45$

Calculation of molecular mass :

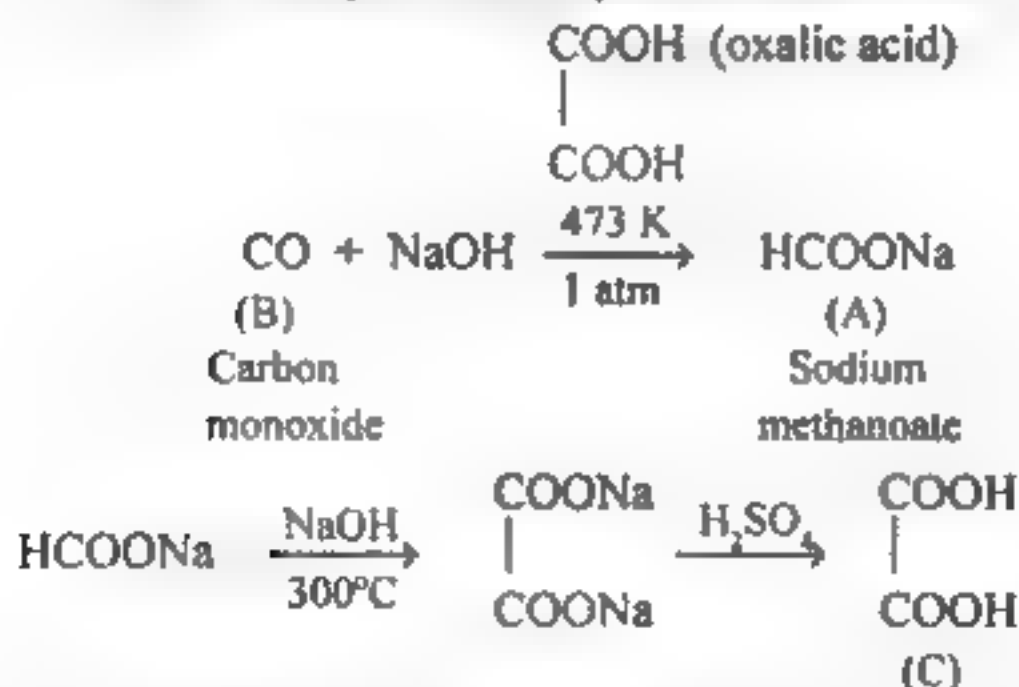
$$\begin{aligned} \text{Equivalent mass of the acid} &= \left(\frac{\text{Mass of Ag salt}}{\text{Mass of Ag}} \times 108 \right) - 107 \\ &= \left(\frac{100 \text{ g}}{0.71 \text{ g}} \times 108 \right) - 107 = 45 \end{aligned}$$

$$\begin{aligned} \text{Molecular mass of the acid} &= \text{Equivalent mass} \times \text{Basicity} \\ &= 45 \times 2 = 90 \text{ g/mol} \end{aligned}$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{90}{45} = 2$$

∴ Molecular formula of the acid = $2 \times \text{CHO}_2 = \text{C}_2\text{H}_2\text{O}_4$.

Since C is a dicarboxylic acid, its probable structure is



Thus A is sodium methanoate, B is carbon monoxide and C is oxalic acid.

Problem 51. Compound (A) $\text{C}_5\text{H}_{12}\text{O}_2$ on reduction with LiAlH_4 yielded two compounds (B) and (C). The compound (B) on oxidation gave (D) which on treatment with aqueous alkali and subsequent heating furnished (E). The latter on catalytic hydrogenation gave (C). The compound (D) was oxidized further to give (F) which was found to be a monobasic acid (molecular formula weight = 60.0). Deduce the structures of (A), (B), (C), (D) and (E).

[IIT/JEE 91]



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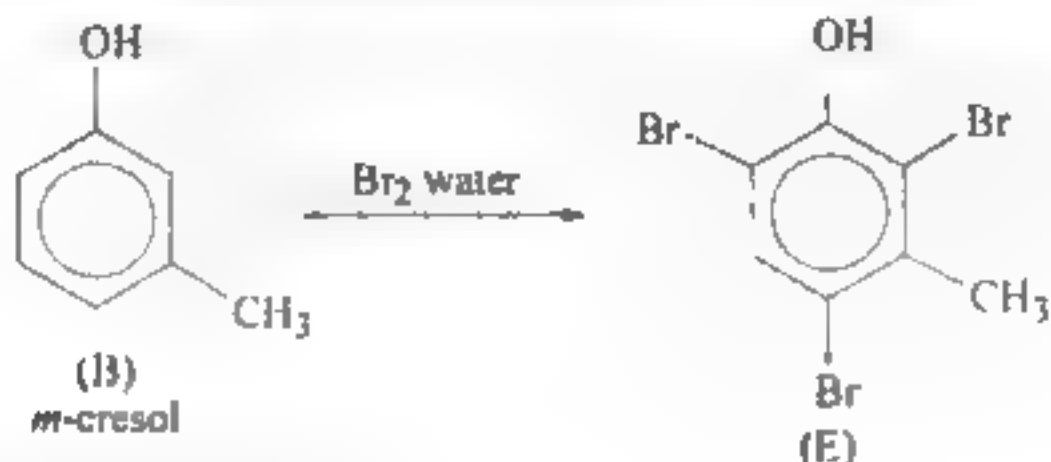
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Calculation of empirical formula :

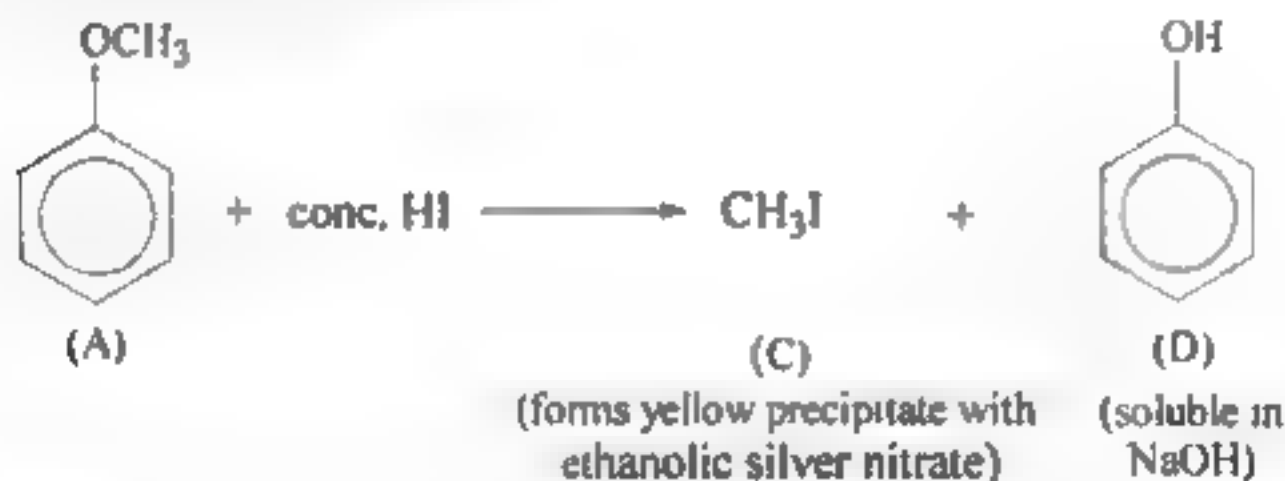
| Element | Percentage | Atomic mass | Relative number of atoms | Divided by lowest number | Simple ratio |
|---------|------------|-------------|---------------------------|--------------------------|--------------|
| C | 77.77 | 12 | $\frac{77.77}{12} = 6.48$ | $\frac{6.48}{0.92} = 7$ | 7 |
| H | 7.4 | 1 | $\frac{7.4}{1} = 7.4$ | $\frac{7.4}{0.92} = 8$ | 8 |
| O | 14.83 | 16 | $\frac{14.83}{16} = 0.92$ | $\frac{0.92}{0.92} = 1$ | 1 |

∴ The empirical formula of the compound is C_7H_8O

Since *B* is soluble in NaOH and readily reacts with bromine water to form $C_7H_5OBr_3$, compound *B* is a phenol. As the compound *E* contains 3 Br atoms, they must be at 2, 4 and 6 positions because —OH group is ortho and para-directing in electrophilic substitution.

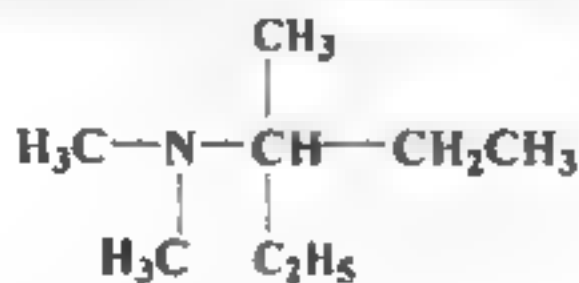


The isomer of *B* should be an ether.

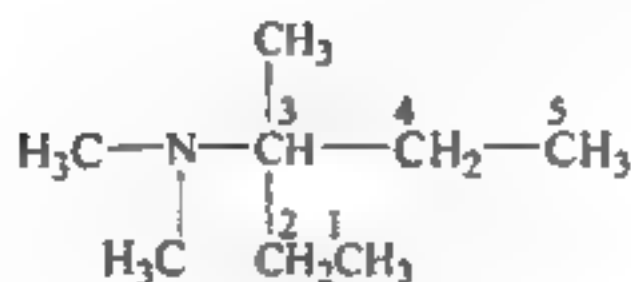


Problem 56. Write the IUPAC name for the following :

[IIT/JEE 91]



Solution.



3-(N,N-dimethyl amino)-3-methyl pentane



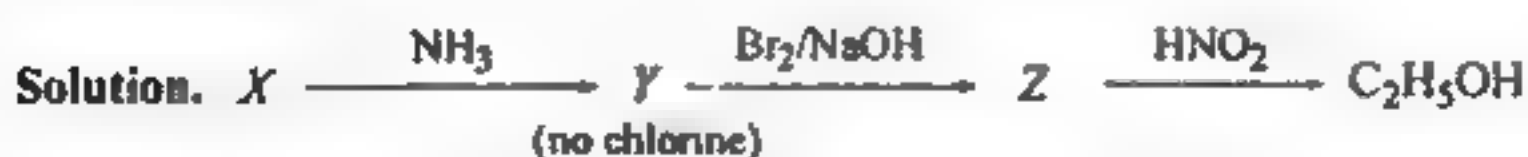
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These reactions suggest that Z is an amine, Y is an amide and X is an acid chloride. In ethanol, alkyl group is C_2H_5- and therefore X is C_2H_5COCl .

Determination of Molecular Formula of Y :

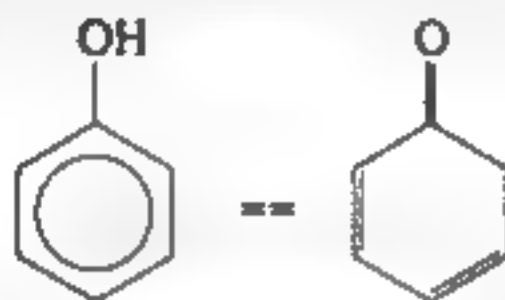
| Element | % of atoms | Relative number | Simple ratio |
|---------|--|--------------------------|------------------------|
| C | 49.31 | $\frac{49.31}{12} = 4.1$ | $\frac{4.1}{1.3} = 3$ |
| H | 9.59 | $\frac{9.59}{1} = 9.59$ | $\frac{9.59}{1.3} = 7$ |
| N | 19.18 | $\frac{19.18}{14} = 1.3$ | $\frac{1.3}{1.3} = 1$ |
| O | $100 - (49.31 + 9.59 + 19.18) = 21.92$ | $\frac{21.92}{16} = 1.3$ | $\frac{1.3}{1.3} = 1$ |

The empirical formula of Y is C_3H_7NO . This suggests that Y is $C_3H_7CONH_2$.

Problem 68. Write tautomeric forms for phenol.

[IIT/JEE 1992]

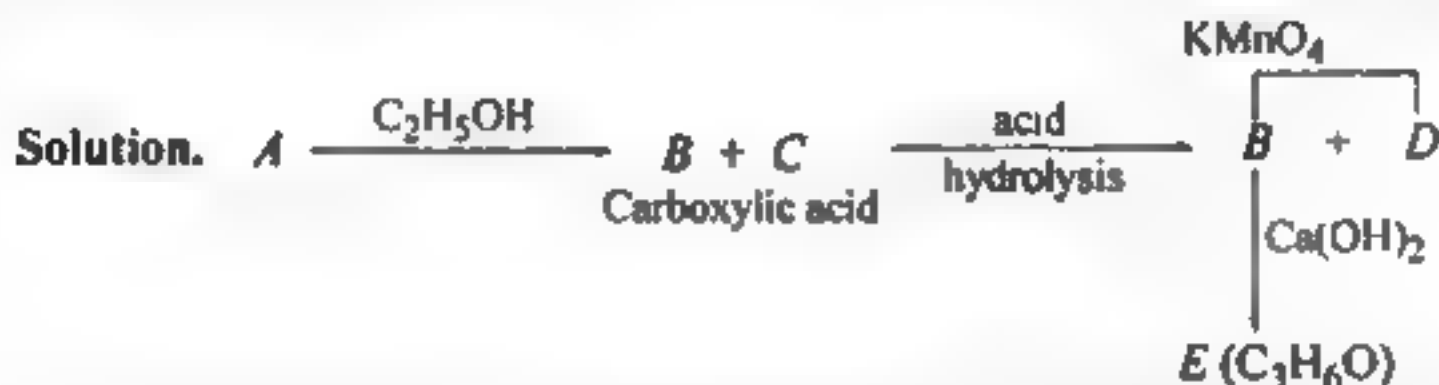
Solution.



Problem 69. An organic compound (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidic conditions give (B) and (D). Oxidation of (D) with KMnO_4 also gives (B). (B) on heating with Ca(OH)_2 gives (E) (molecular formula, $\text{C}_3\text{H}_6\text{O}$). (E) does not give Tollen's test and does not reduce Fehling's solution but forms a 2, 4-dinitro phenylhydrazone. Identify (A), (B), (C), (D) and (E).

[IIT/JEE 1992]

[IIT/JEE 1992]



(1) *E* does not give Tollen's test and does not reduce Fehling's solution but forms 2, 4-dinitro phenylhydrazone. Therefore, *E* is a ketone. $E(C_3H_6O)$ is acetone CH_3COCH_3 .

(ii) Since E is obtained by heating B with $\text{Ca}(\text{OH})_2$, B must be a carboxylic acid. B is acetic acid (CH_3COOH).

(iii) As *B* is obtained by the oxidation of *D*, therefore, *D* is ethanol, ($\text{C}_2\text{H}_5\text{OH}$).

(iv) *C* is therefore an ester, ethyl acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$.

(v) Since *A* on treatment with ethyl alcohol gives acetic acid and ethyl acetate, *A* is acetic anhydride.



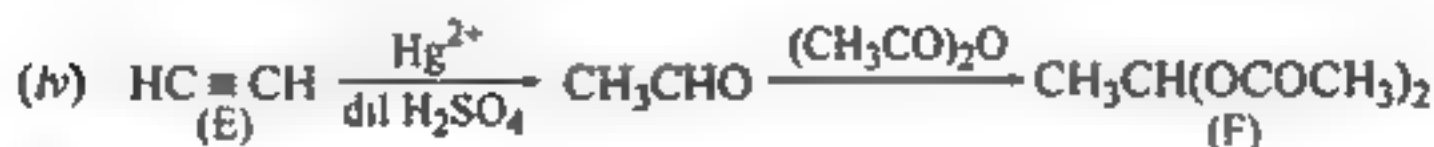
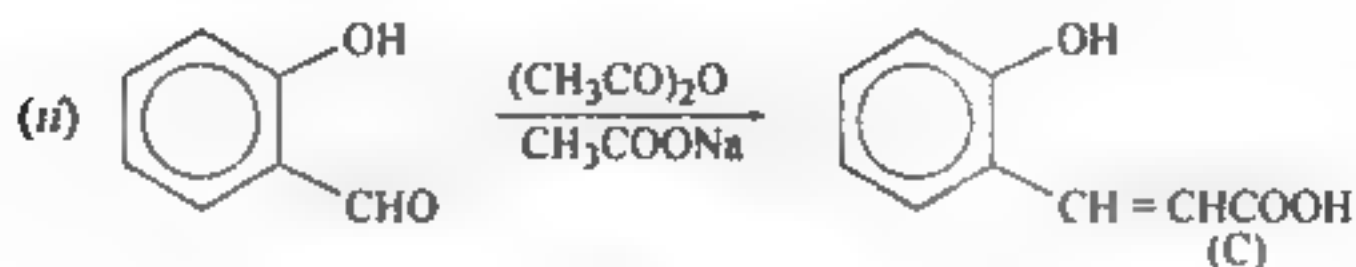
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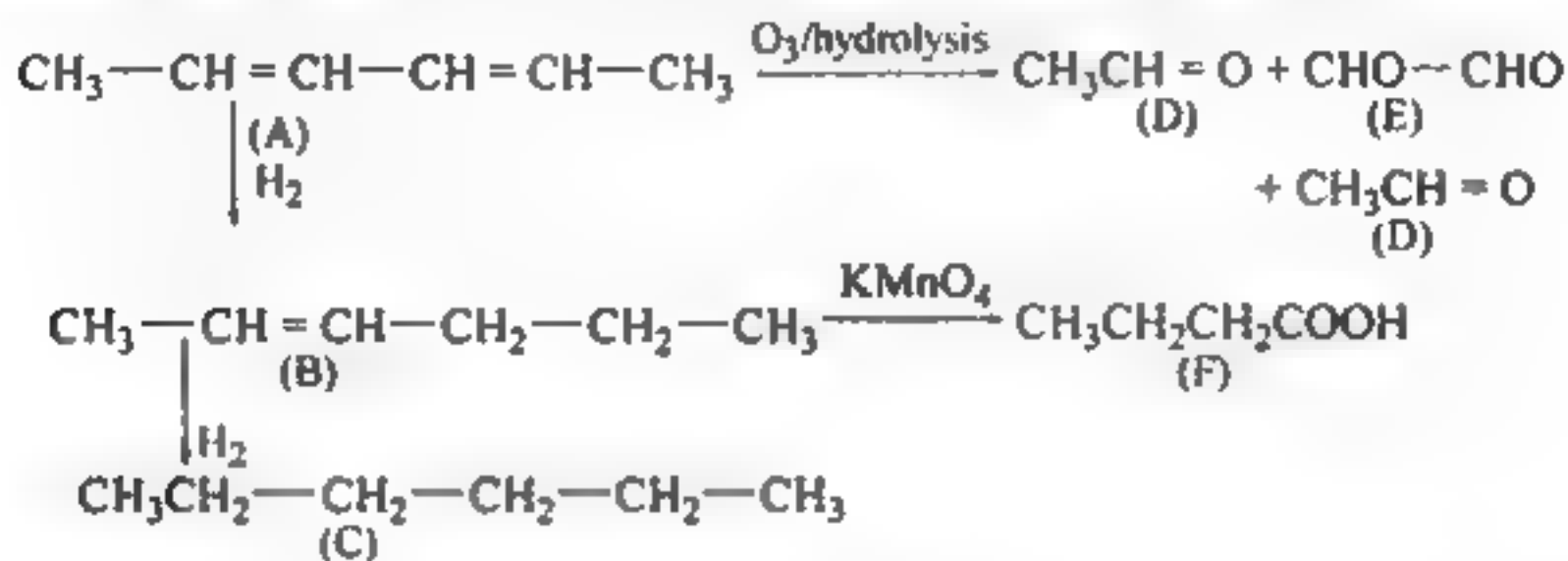
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Problem 75. An organic compound (A), C_6H_{10} , on reduction first gives (B), C_6H_{12} , and finally (C), C_6H_{14} . (A) on ozonolysis followed by hydrolysis gives two aldehydes (D), C_2H_4O , and (E) $C_2H_2O_2$. Oxidation of (B) with acidified $KMnO_4$ gives the acid (F), $C_4H_8O_2$. Determine the structures of the compounds (A) to (F) with proper reasoning.

[Roorkee 93]

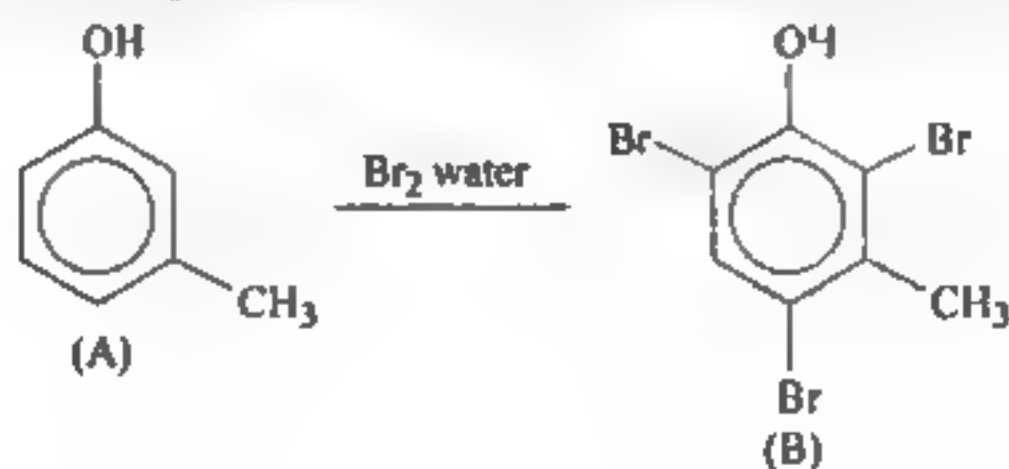
Solution. As ozonolysis of compound *A* followed by hydrolysis gives two aldehydes (and no carboxylic acids), *A* contains double bonds. Reduction of *A* takes place in two steps, therefore *A* contains two double bonds. *A* is an alkadiene *C* is a saturated compound and *B* contains one double bond. Formation of two molecules of CH_3CHO ($\text{C}_2\text{H}_4\text{O}$) indicates that *A* must contain $\text{CH}_3\text{—CH=CH—}$ groups. Therefore, compound *A* is



Problem 76. An organic compound (A), C_7H_8O , is insoluble in aqueous $NaHCO_3$ but soluble in $NaOH$. (A) on treatment with bromine water rapidly forms compound (B), $C_7H_5OBr_3$. (i) Give structures for (A) and (B). (ii) What will be (A) if it does not dissolve in $NaOH$ but shows reactions given above? Give your answers with proper reasoning.

[Roorkee 93]

Solution. As compound *A* is insoluble in aqueous NaHCO_3 , *A* is not a carboxylic acid but is a phenol as it is soluble in NaOH . Since *A* is brominated to form *B* which contains 3 Br atoms per molecule, CH_3 group is present at *m*-position to the —OH group.





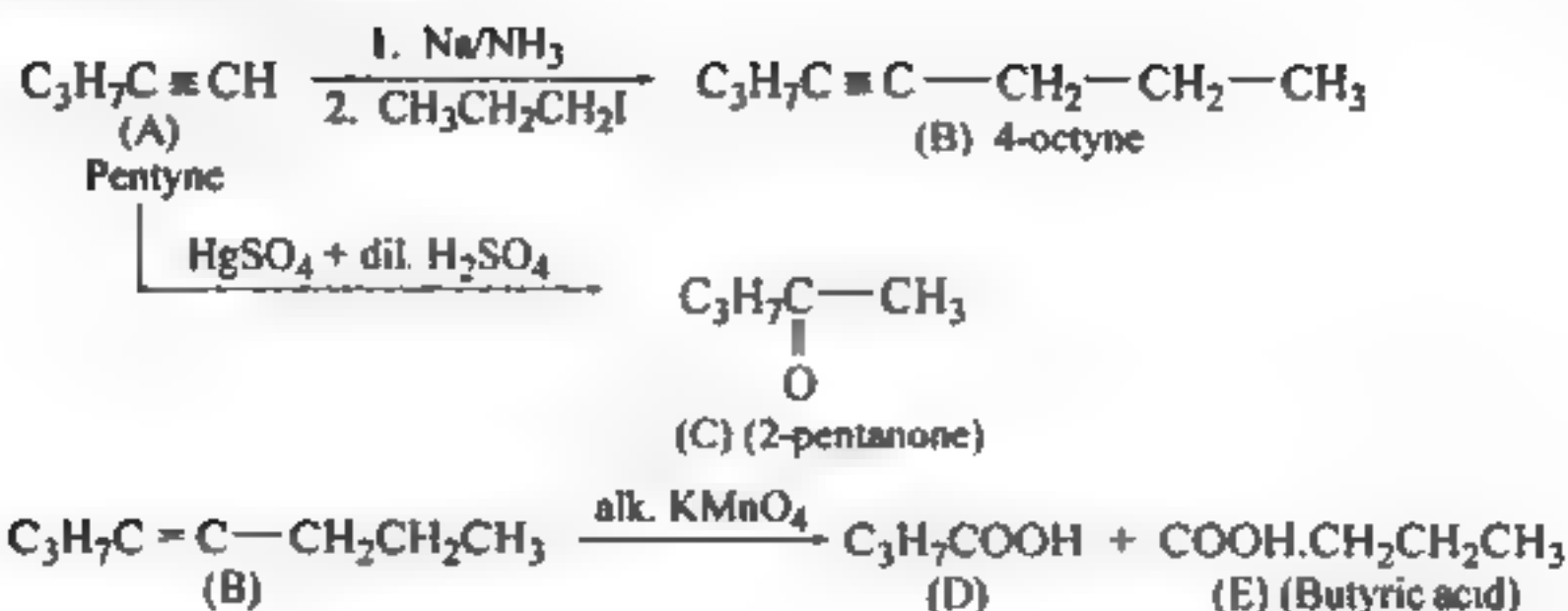
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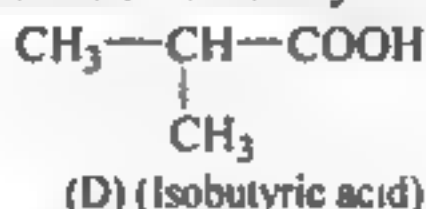


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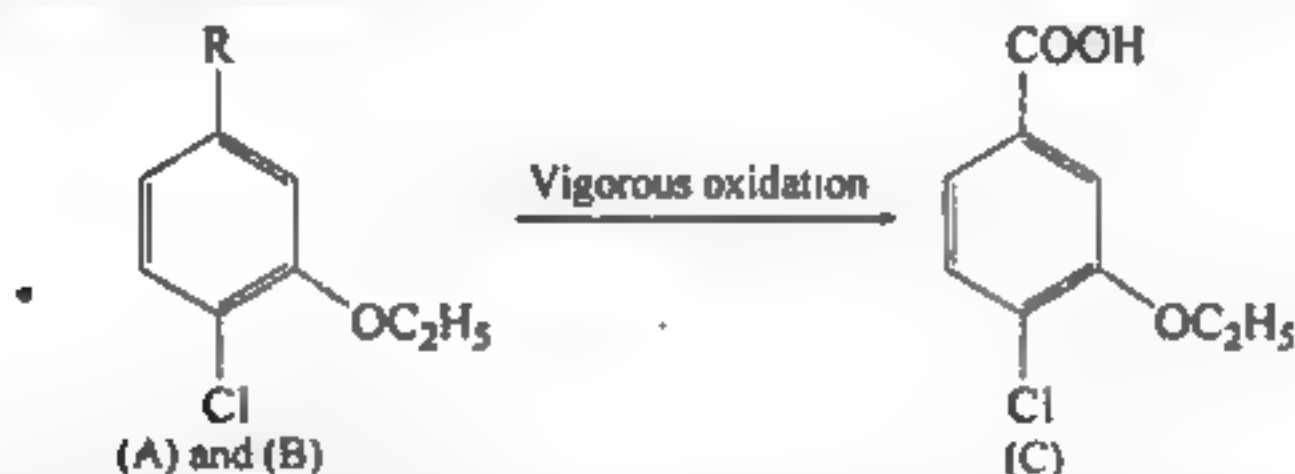
Two isomeric acids

Since *E* is *n*-butyric acid, therefore *D* is isobutyric acid.

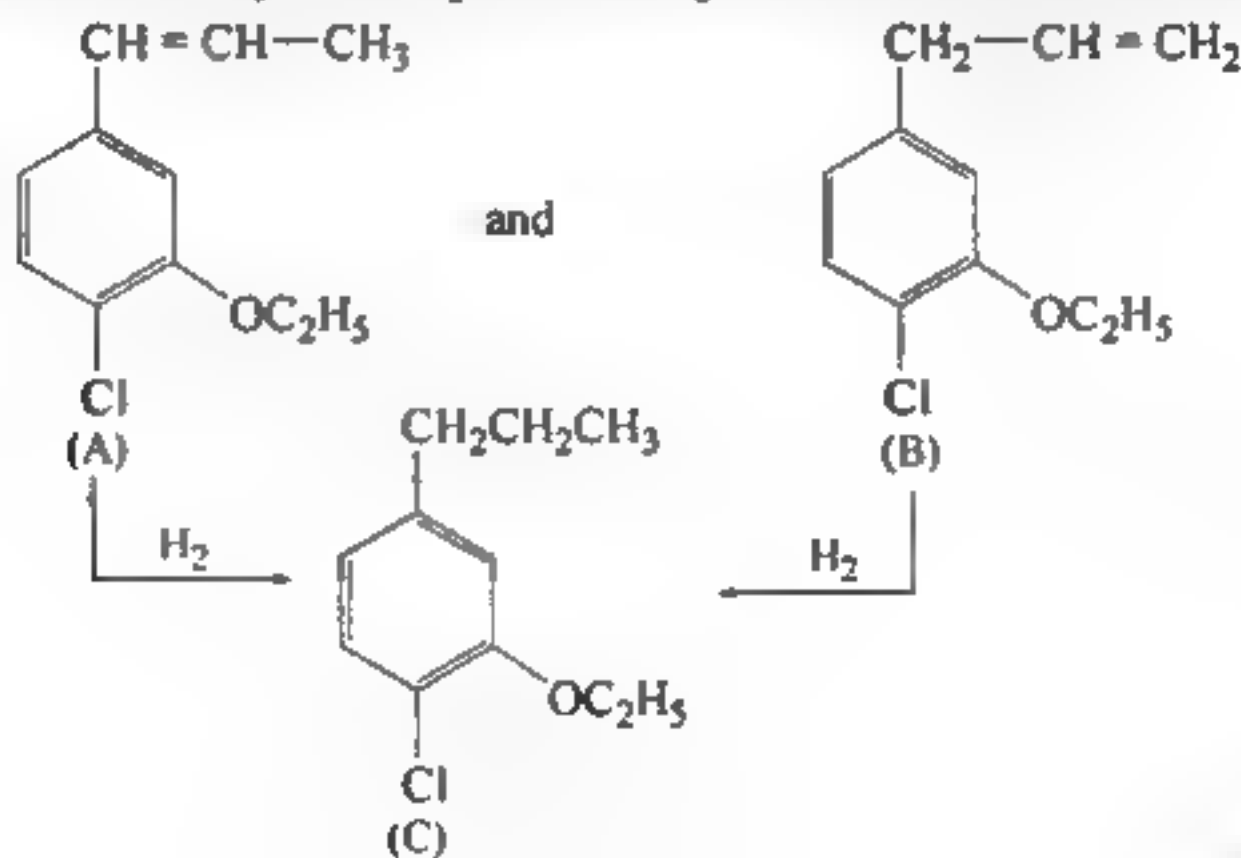


Problem 84. Two isomeric compounds (A) and (B), have the same formula, $\text{C}_{11}\text{H}_{13}\text{OCl}$. Both are unsaturated, yield the same compound (C) on catalytic hydrogenation and produce 4-chloro-3-ethoxybenzoic acid on vigorous oxidation. (A) exists in geometrical isomers, (D) and (E), but not (B). Give structures of (A) to (E) with proper reasoning. [Roorkee 1994]

Solution. As oxidation of *A* and *B* gives 4-chloro-3-ethoxy benzoic acid, the structure of *A* and *B* can be written as



Since the molecular formula of *A* and *B* is $\text{C}_{11}\text{H}_{13}\text{OCl}$, R must be C_3H_5 . As *A* and *B* are unsaturated compounds and both give the same compound C on catalytic hydrogenation, R must be $-\text{CH}=\text{CH}-\text{CH}_3$ or $-\text{CH}_2-\text{CH}=\text{CH}_2$. The structures of *A* and *B*, therefore, are





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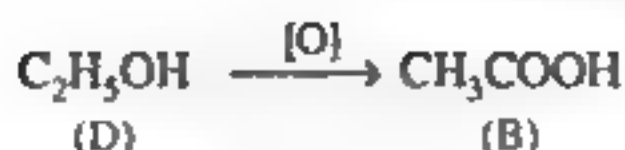
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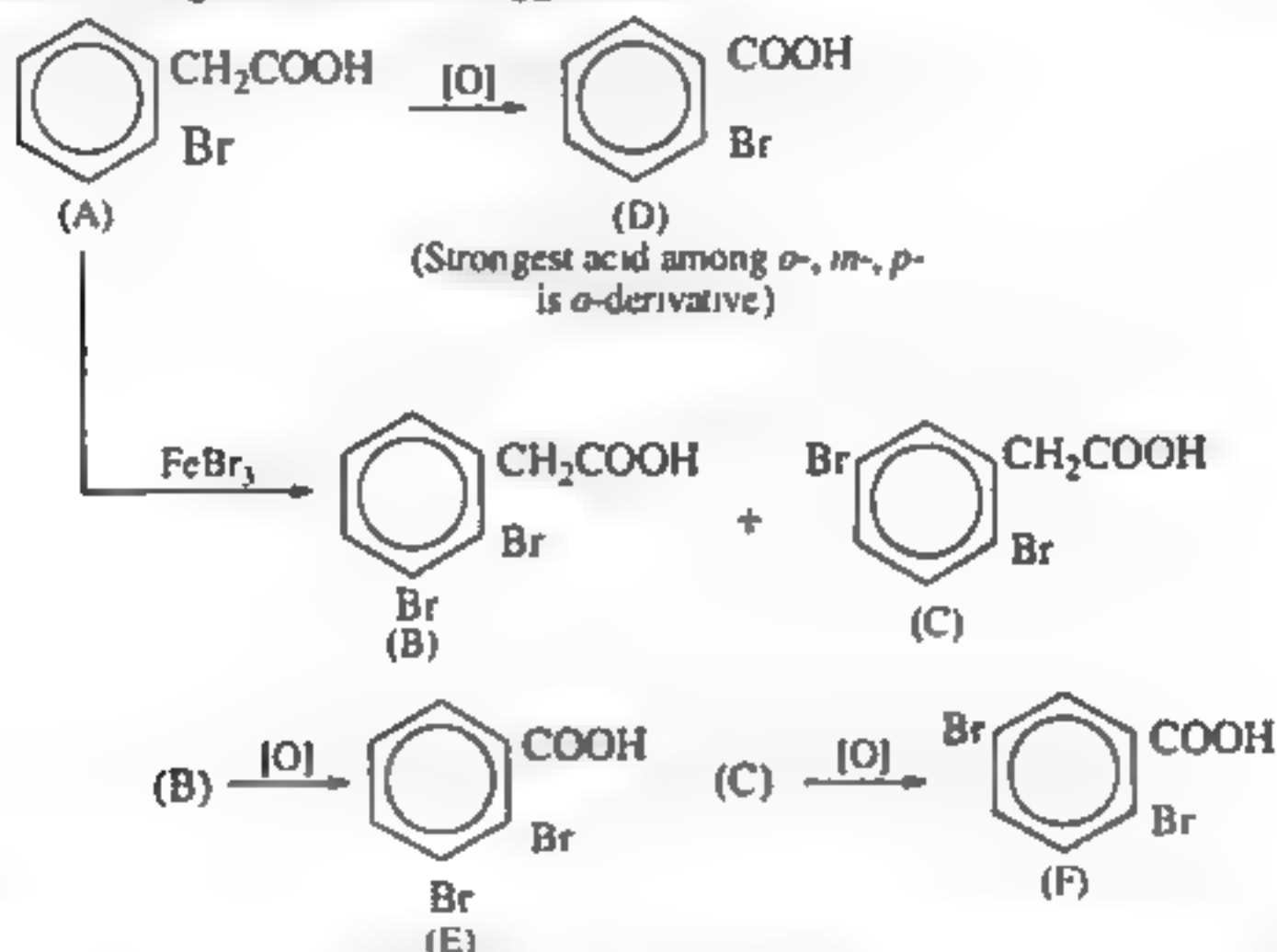


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Problem 134. An acid (A), $\text{C}_8\text{H}_7\text{O}_2\text{Br}$ on bromination in the presence of FeBr_3 gives two isomers, (B) and (C) of formula $\text{C}_8\text{H}_6\text{O}_2\text{Br}_2$. Vigorous oxidation of (A), (B) and (C) gives acids (D), (E) and (F) respectively. (D), $\text{C}_7\text{H}_5\text{O}_2\text{Br}$ is the strongest acid among all of its isomers, whereas (E) and (F) each has a molecular formula of $\text{C}_7\text{H}_4\text{O}_2\text{Br}_2$. Give structures of (A) to (F) with justification. [Roorkee 2000]

Solution. The given reactions suggest that

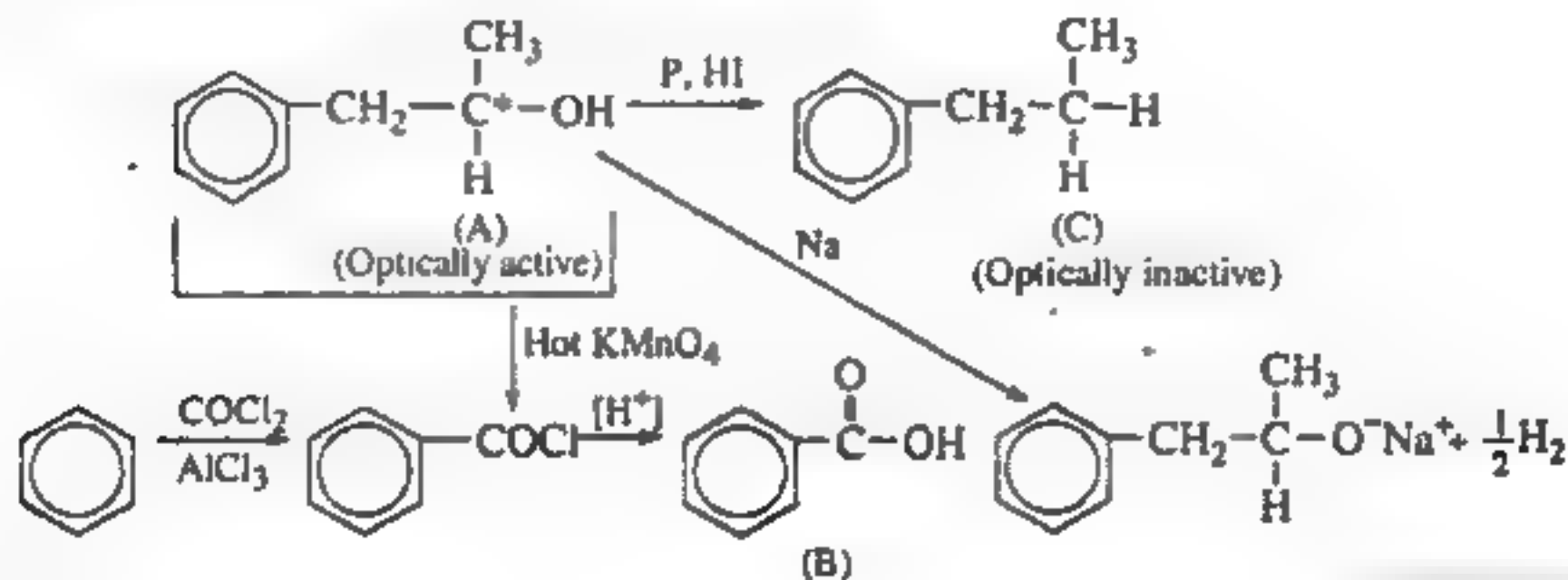


Problem 135. An organic compound (A), $\text{C}_9\text{H}_{12}\text{O}$ was subjected to a series of tests in the laboratory. It was found that this compound : [Roorkee 1999]

- rotates the plane for polarised light.
- evolves hydrogen gas with sodium.
- reacts with I_2 and NaOH to produce a pale yellow solid compound.
- does not react with Br_2/CCl_4 .
- reacts with hot KMnO_4 to form compound (B), $\text{C}_7\text{H}_6\text{O}_2$, which can also be synthesised by the reaction of benzene and carbonyl chloride, followed by hydrolysis.
- loses optical activity as a result of formation of compound (C) on being heated with Lucas reagent in about 5 min.

Give structures of (A) to (C) with proper reasoning and draw Fischer projections for (A). Give reactions for the steps wherever possible.

Solution.





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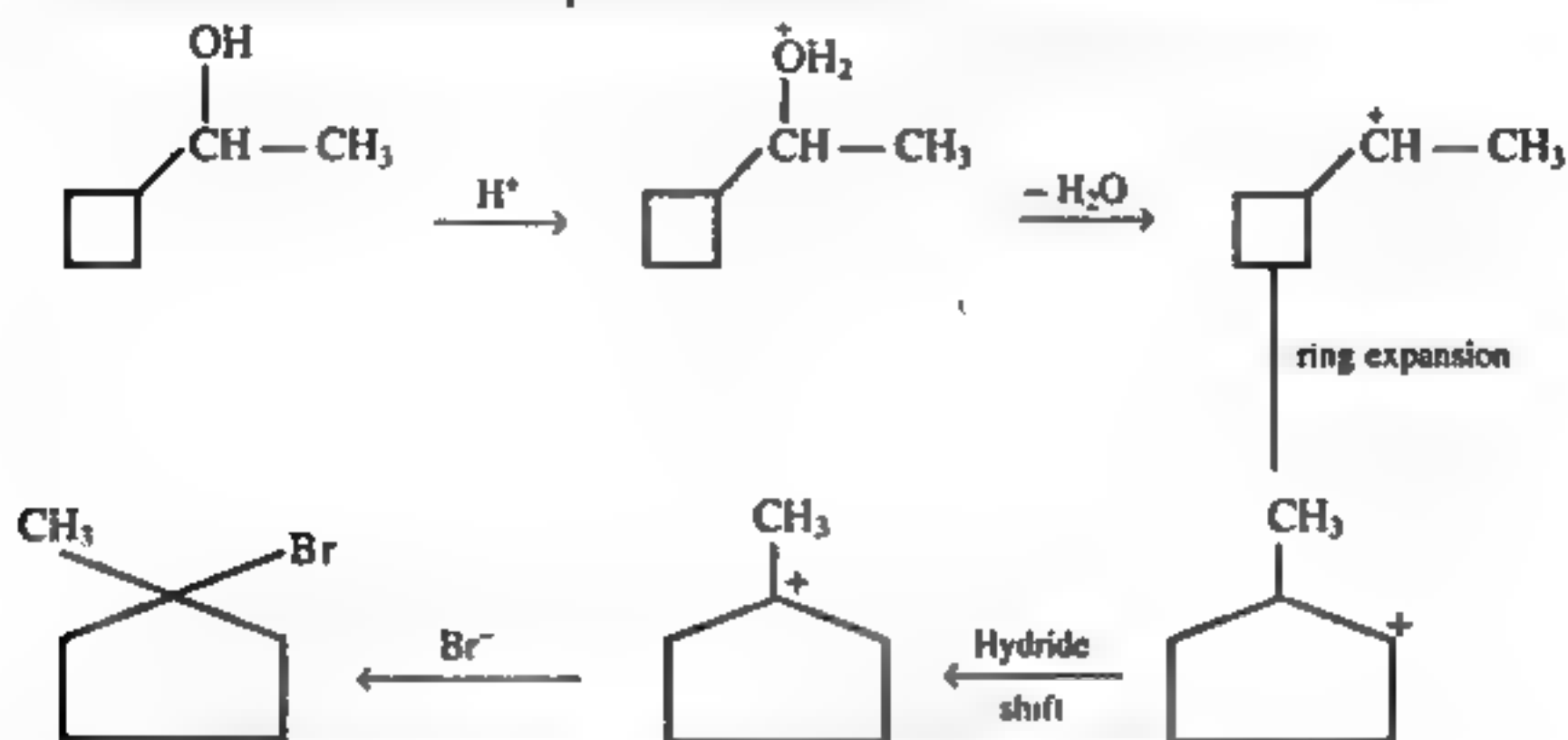


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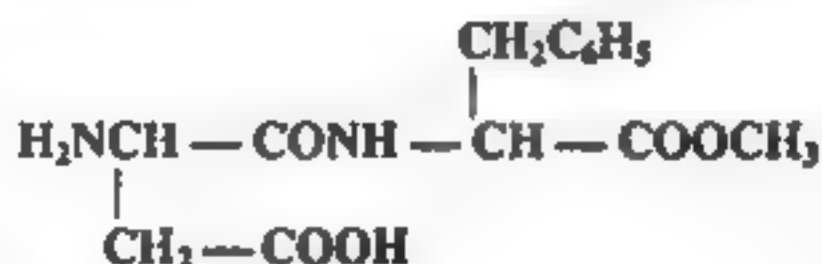
The formation of C from B proceeds as follows :



Ring expansion occurs due to more stable five-membered ring.

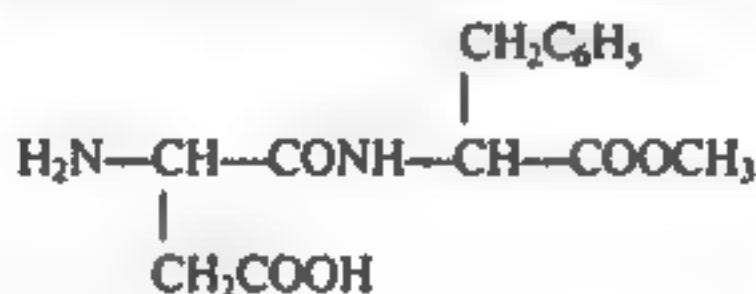
Hydride shift occurs due to more stable 3° carbocation.

Problem 148. Aspartame, an artificial sweetener, is a peptide and has the following structure :



- (i) Identify the four functional groups.
- (ii) Write the zwitter-ionic structure.
- (iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
- (iv) Which of the two amino acids is more hydrophobic? (IIT/JEE 2001)

Solution. (i) The given compound, aspartame, is



The four functional groups in this compound are

- | | |
|------------------------|-----------------------------------|
| (a) an amine group | $-\text{NH}_2$ |
| (b) a carboxylic group | $-\text{COOH}$ |
| (c) an amide group | $-\text{C}(=\text{O})-\text{NH}-$ |
| (d) an ester group | $-\text{C}(=\text{O})-\text{O}-$ |



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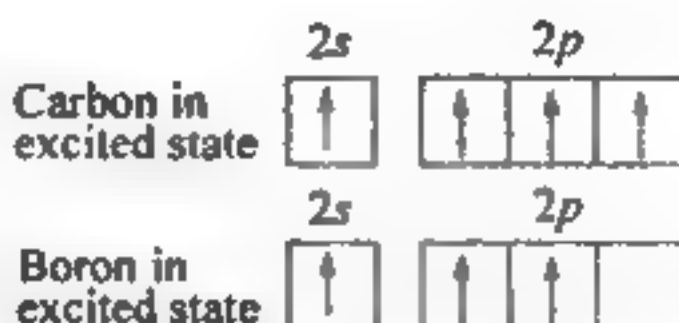


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the first electron from carbon atom is removed from exactly half-filled $2p$ orbitals which have extra-stability.



The second ionization energy of boron is higher than that of carbon because B^+ has a smaller size than C^+ .

(ii) H_3PO_3 (phosphorus acid) is a dibasic acid because the two hydrogen atoms bonded to oxygen atoms are ionizable whereas the third hydrogen atom bonded directly to phosphorus atom is non-ionizable.

(iii) Phosphine has lower boiling point than ammonia because phosphorus is less electronegative than nitrogen and, therefore, hydrogen bonding between phosphine molecules is practically negligible.

Problem 12. Write the two resonance structures of N_2O that satisfy the octet rule.

[IIT/JEE 1990]

Solution. Resonance structures of nitrous oxide



Problem 13. Arrange the following as stated :

[IIT/JEE 1991]

- (i) Increasing order of ionic size
[N^{3-} , Na^+ , F^- , O^{2-} , Mg^{2+}]
- (ii) Increasing order of acid strength
[MgO , SrO , K_2O , NiO , Cs_2O]
- (iii) Increasing order of acid strength
[$ClCH_2COOH$, CH_3CH_2COOH , $ClCH_2CH_2COOH$,
 $(CH_3)_2CHCOOH$, CH_3COOH]
- (iv) Increasing order of extent of hydrolysis
[CCl_4 , $MgCl_2$, $AlCl_3$, PCl_5 , $SiCl_4$]
- (v) Increasing strength of hydrogen bonding ($X \cdots H - X$)
[O, S, F, Cl, N]

Solution. (i) $Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$

All these ions are isoelectronic. Higher the atomic number, smaller is the ionic size.

(ii) $Ni_2O < MgO < SrO < K_2O < Cs_2O$.

Alkaline metal oxides are highly basic and basic character increases down the group.

(iii) $(CH_3)_2CHCOOH < CH_3CH_2COOH < CH_3COOH < ClCH_2CH_2COOH$
 $< ClCH_2COOH$. CH_3 group is electron releasing and Cl group is electron withdrawing.

(iv) $CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$

Si and P atoms have empty d -orbitals and form oxy-acids

(v) $S < Cl < N < O < F$



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Problem 37. Interpret the non-linear shape of H_2S molecule and non-planar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory. [IIT/JEE 1998]

(Atomic numbers : $\text{H} = 1$, $\text{P} = 15$, $\text{S} = 16$; $\text{Cl} = 17$)

Solution. In H_2S , number of lone pairs around sulphur atom = 2

No. of Bond pairs around sulphur atom = 2

H_2S has V-shape because repulsions between lone pair—lone pair is greater than between a lone-pair—bond pair which in turn is greater than between bond pair—bond pair. In PCl_3 , No. of lone pairs + bond pairs = $1 + 3 = 4$.

$\therefore \text{PCl}_3$ has pyramidal shape.

Problem 38. Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H_2O_2 using chemical equations. [IIT/JEE 1998]

Solution. Oxidising agent $\text{H}_2\text{O}_2 + 2e^- \longrightarrow 2\text{OH}^-$

In basic medium $\text{Cr}(\text{OH})_3$ is oxidised to CrO_4^{2-}



Reducing agent $\text{H}_2\text{O}_2 + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 2e^-$

Alkaline solution of ferricyanide is reduced to Ferrocyanide



Problem 39. Match the following choosing one item from Column X and the appropriate item from Column Y. [Roorkee 2000]

X

Y

(A) SO_2Cl_2

(i) Paramagnetic

(B) Ice

(ii) Refrigeration

(C) CuSO_4 (anhydrous)

(iii) Testing NH_3

(D) $\text{K}_2\text{HgI}_4 + \text{NaOH}$

(iv) Testing H_2O

(E) Fluorocarbons

(v) Hydrogen bonding

(F) NO

(vi) Tetrahedral

Solution. A (vi) ; (B) (v) ; (C) (iv) ; (D) (iii) ; (E) (ii) ; (F) (i)

Problem 40. Give reasons for the following :

(i) The solubility of calcium acetate decreases while that of lead nitrate increases with increase in temperature.

(ii) Magnesium is not precipitated from a solution of its salt by NH_4OH in the presence of NH_4Cl

(iii) Yellow phosphorus is kept under water but not the red phosphorus.

(iv) Bleaching of flowers with SO_2 gas is temporary while that with Cl_2 gas is permanent. [Roorkee 2000]



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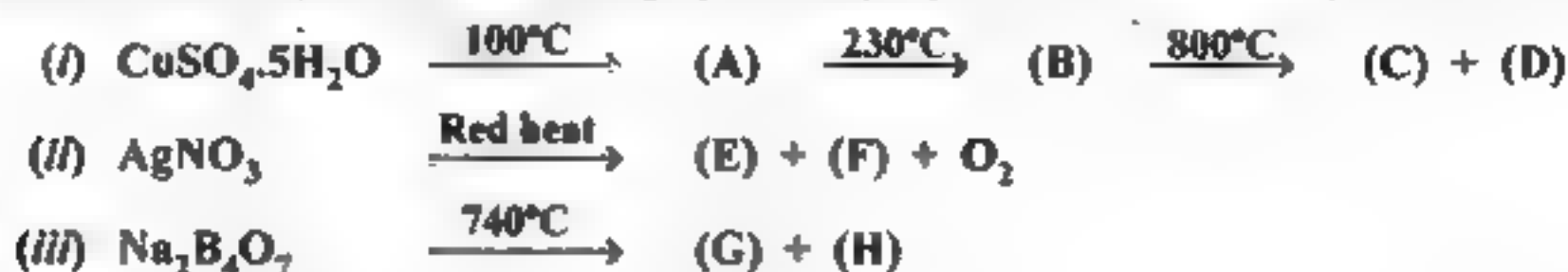


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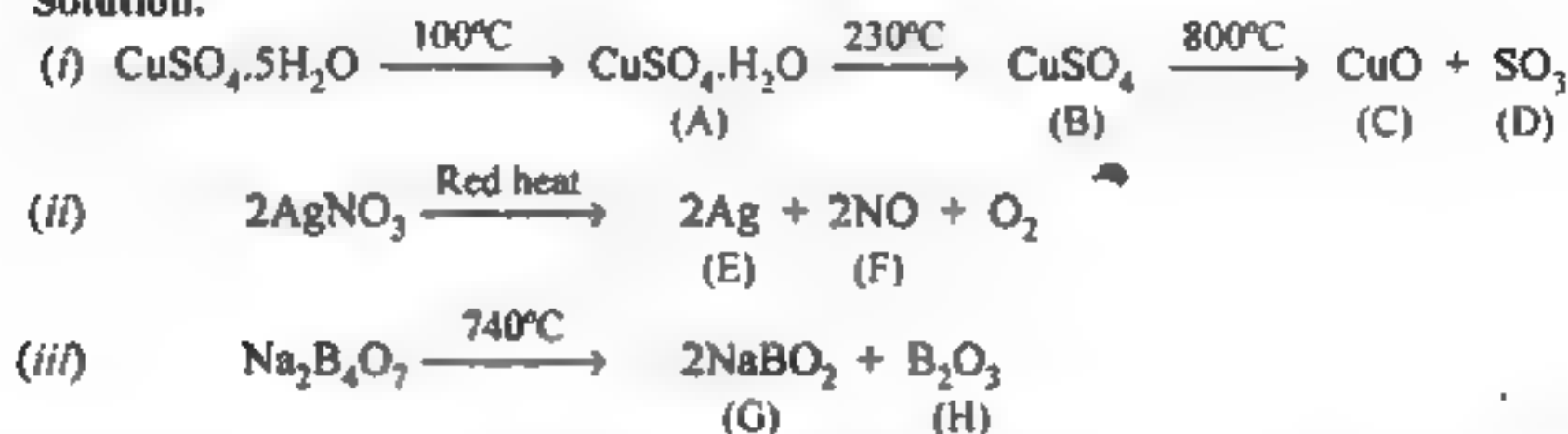


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Problem 16. Complete the following by identifying (A) to (H). [Roorkee 2000]

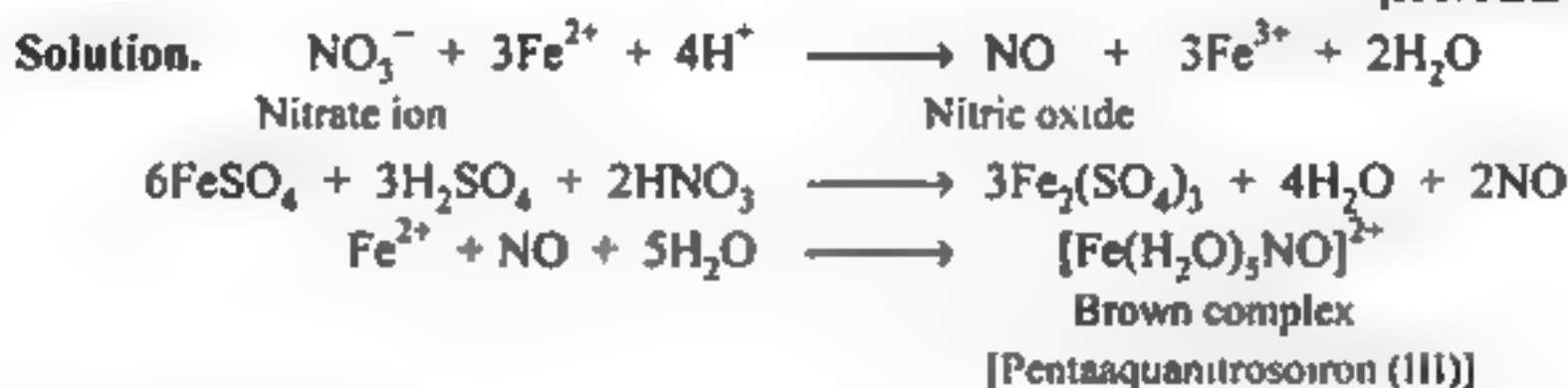


Solution.



Problem 17. Write the chemical reactions associated with the 'brown ring test'.

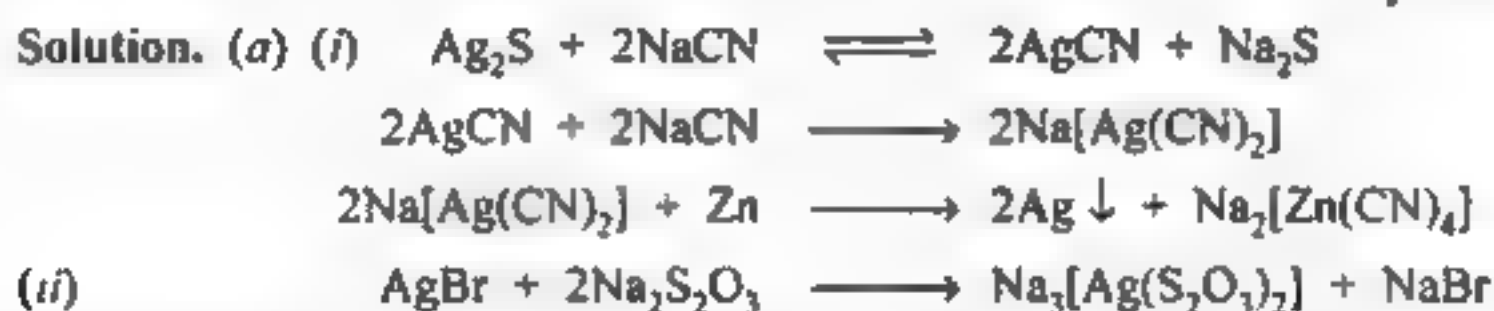
[IIT/JEE 2000]



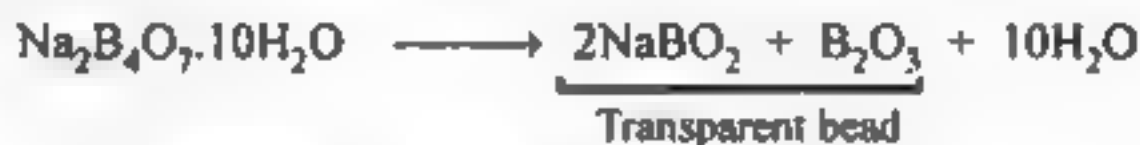
Problem 18. (a) (i) Write the chemical reactions involved in the extraction of metallic silver from argentite.

(ii) Write the balanced chemical equation for developing photographic films.

(b) Write the chemical reactions associated with borax bead test of cobalt (II) oxide. [IIT/JEE 2000]



(b) When powdered borax is heated strongly in a bunsen flame, it loses its water of crystallization and forms colourless transparent glass bead which is made of sodium metaborate and boric anhydride.



Cobalt oxide with Boric anhydride in oxidising as well as reducing flame gives blue colour.



Problem 19. Complete and balance the following chemical equations :





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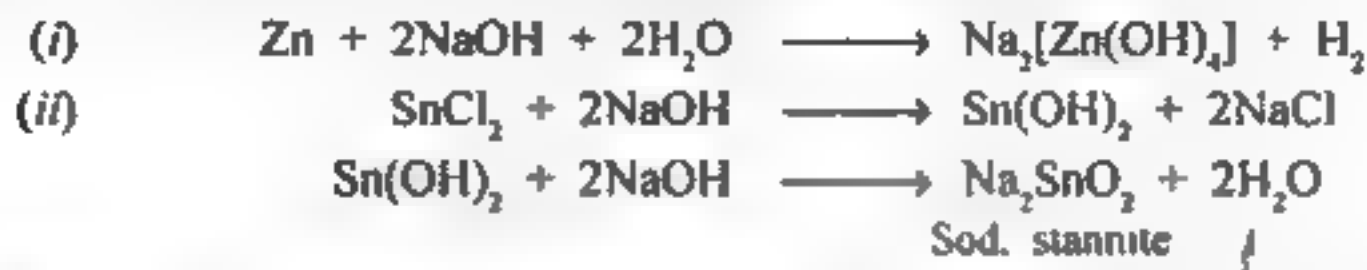


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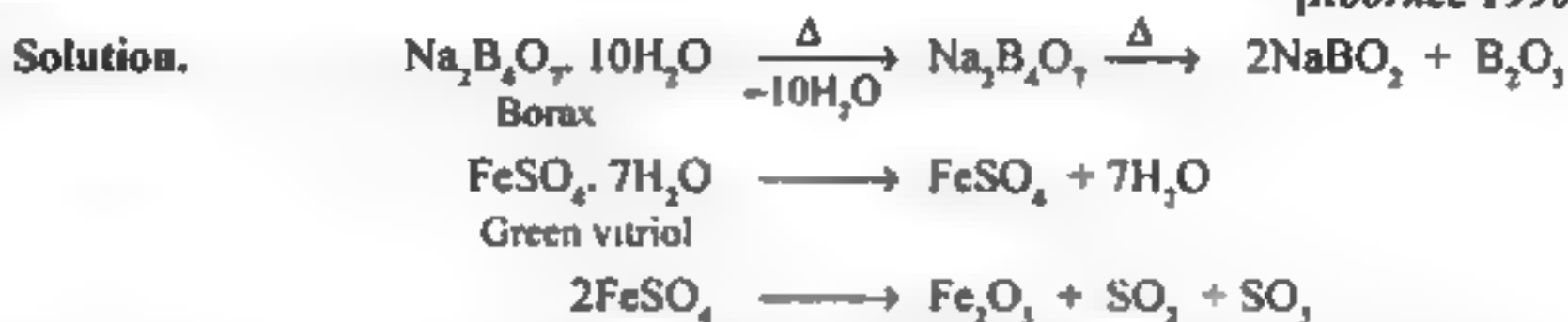


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Solution. X is sodium compound because sodium imparts golden yellow flame. Since zinc powder evolves hydrogen with aqueous solution of X , X is sodium hydroxide.

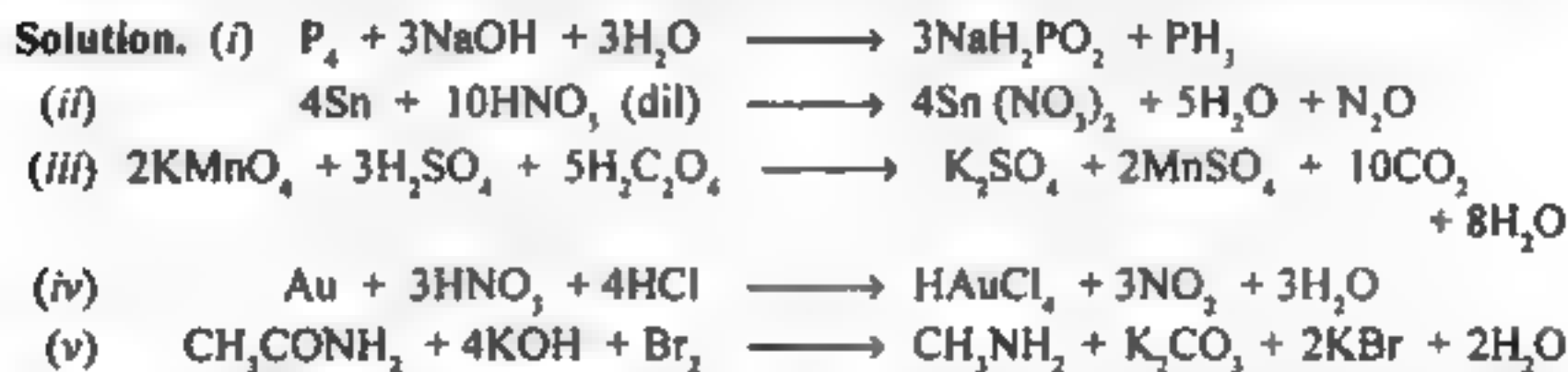


Problem 12. Write equations for the action of strong heat on borax and green vitriol. [Roorkee 1990]

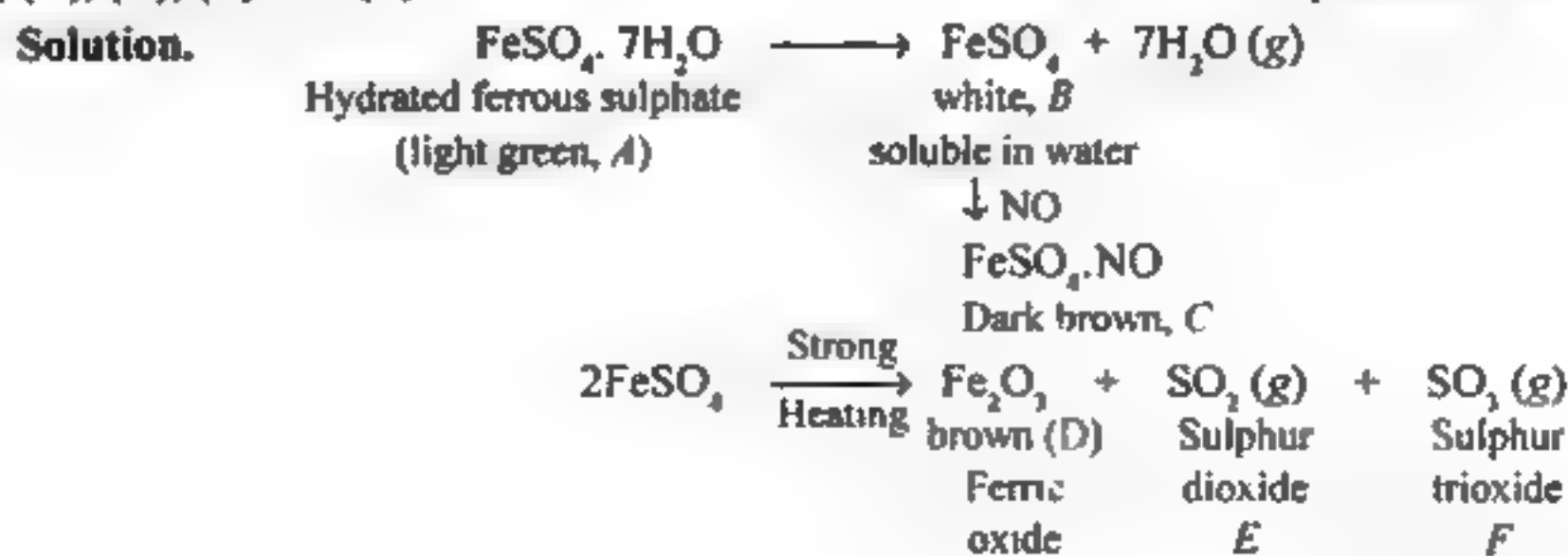


Problem 13. Write balanced equations for the following reactions : [IIT/JEE 1987]

- Phosphorus is reacted with boiling aqueous solution of sodium hydroxide in an inert atmosphere.
- Dilute nitric acid is slowly reacted with metallic tin.
- Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid.
- Gold is dissolved in *aqua regia*.
- Acetamide is reacted with bromine in the presence of potassium hydroxide.



Problem 14. A hydrated metallic salt (A), light green in colour, gives a white anhydrous residue (B) after being heated gradually. (B) is soluble in water and its aqueous solution reacts with NO to give a dark brown compound (C). (B) on strong heating gives a brown residue (D) and a mixture of two gases (E) and (F). The gaseous mixture, when passed through acidified permanganate, discharges the pink colour and when passed through acidified BaCl_2 solution, gives a white precipitate. Identify (A), (B), (C), (D), (E) and (F). [IIT/JEE 1988]





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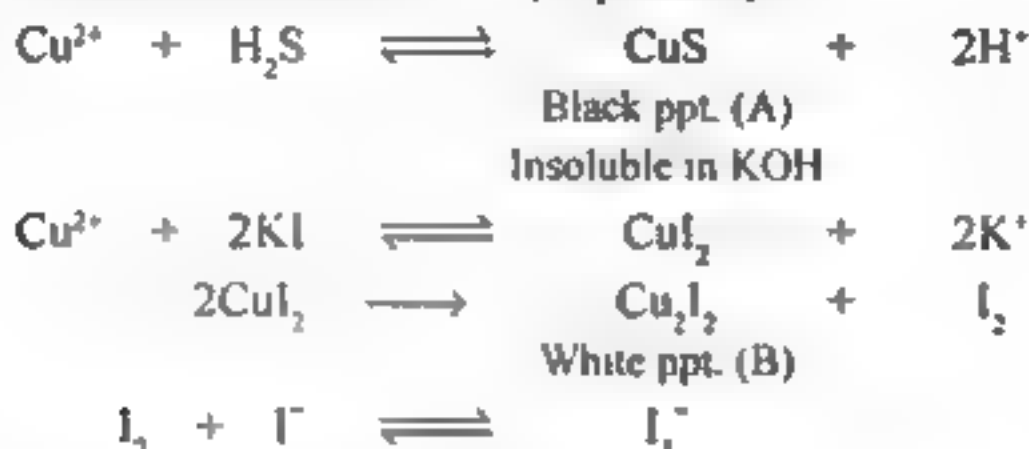
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(c) Hydrogen bonding present in *o*-hydroxybenzaldehyde is *intramolecular*; while in *p*-hydroxybenzaldehyde it is *intermolecular*.

Problem 58. An aqueous blue coloured solution of a transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate (A), which is insoluble in warm aqueous solution of KOH . The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate (B). Identify the transition metal ion. Write the chemical equations in the formation of (A) and (B).

[IIT/JEE 2000]

Solution. Transition metal ion is Cu^{2+} (Cupric ion).



Problem 59. (i) An ore (A) on roasting with sodium carbonate and lime in the presence of air gives two compounds (B) and (C).

(ii) The solution of (B) in conc. HCl on treatment with Potassium ferrocyanide gives a blue colour or precipitate of compound (D).

(iii) The aqueous solution of (C) on treatment with conc. H_2SO_4 gives a yellow coloured compound (E).

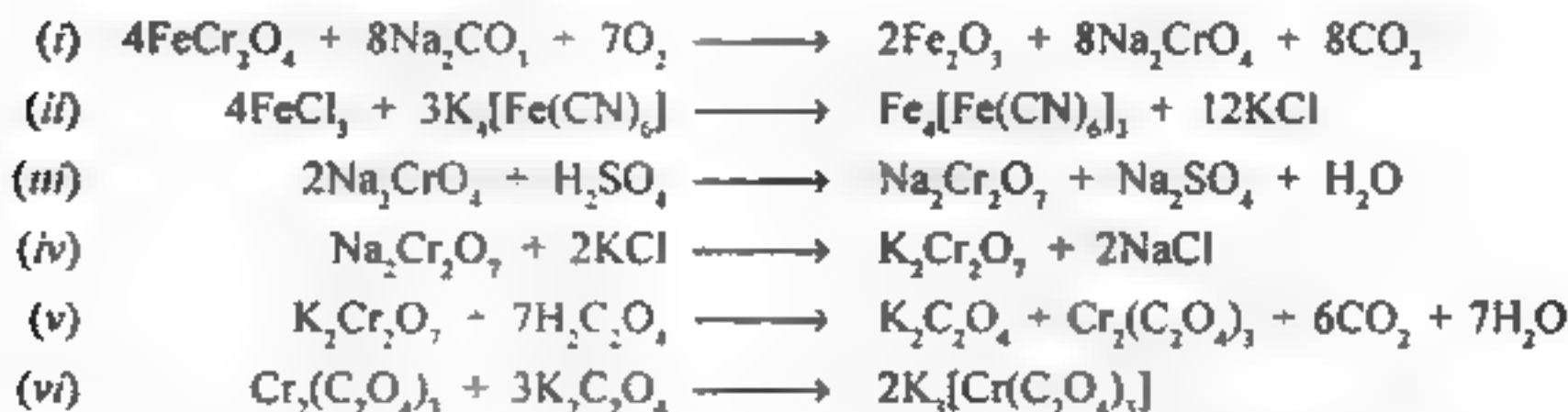
(iv) Compound (E) when treated with KCl gives an orange-red compound (F) which is used as an oxidising reagent.

(v) The solution of (F) on treatment with oxalic acid and then with an excess of potassium oxalate gives blue crystals of compound (G).

Identify (A) to (G) and give balanced chemical equations for reactions at steps (i) to (v). [Roorkee 2000]

Solution. (A) FeCr_2O_4 or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ (E) $\text{Na}_2\text{Cr}_2\text{O}_7$ (yellow)
 (B) Fe_2O_3 (F) $\text{K}_2\text{Cr}_2\text{O}_7$ (orange-red)
 (C) Na_2CrO_4 (G) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ (blue)
 (D) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (blue)

The reactions involved are :



Problem 60. (A), (B) and (C) are three complexes of chromium (III) with the empirical formula $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$. All the three complexes have water and chloride ion as ligands. Complex (A) does not react with concentrated H_2SO_4 ; whereas complexes (B) and (C)



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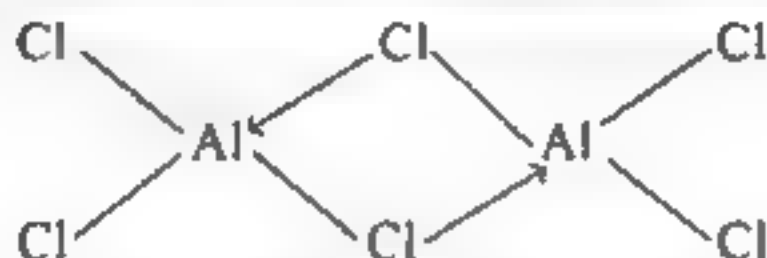
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- (iii) The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markownikoff's rule. The catalyst does not affect the energy of activation in a chemical reaction.

Ans : (i) **False.** Al_2Cl_6 has a bridge structure in which Al—Cl bonds of terminal chlorine atoms are different from those of bridge chlorine atoms.



- (ii) **False.** Ferrocyanide ion is diamagnetic (no unpaired electron) while ferricyanide ion is paramagnetic (one unpaired electron).
 (iii) **False.** This is an example of Markownikoff's rule. The catalyst lowers the energy of activation in a chemical reaction.

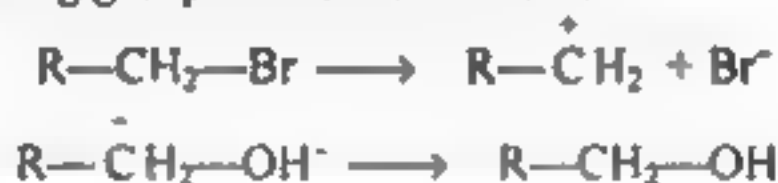
Q. 3. Giving reasons in brief, indicate whether the following statements are True or False. (IIT/JEE 1990)

- (i) The presence of polar bonds in a polyatomic molecule suggest that the molecule has a non-zero dipole moment.
 (ii) 2, 3, 4-Trichloropentane has three asymmetric carbon atoms.
 (iii) During $\text{S}_{\text{N}}1$ reaction the leaving group leaves the molecule before the incoming group is attached to the molecule.
 (iv) In β -emission from a nucleus the atomic number of the daughter element decreases by one.
 (v) The rate of an exothermic reaction increases with increasing temperature.

Ans : (i) **False.** If the dipoles cancel each other exactly as in CCl_4 , the molecule has zero dipole moment.

(ii) **False.** 2, 3, 4-trichloropentane has 1 asymmetric carbon atom. There is only 1 possibility in which four different groups are attached to a carbon atom.

(iii) **True.** $\text{S}_{\text{N}}1$ reaction occurs in two steps. A carbonium ion is formed in the first step when leaving group leaves the molecule.



(iv) **False.** In β -emission from a nucleus the atomic number of the daughter element increases by 1 because when a neutron breaks up to emit an electron, a proton is formed.

(v) **False.** The rate of a reversible exothermic reaction decreases with increasing temperature because the equilibrium is shifted to the left. The rate of an irreversible exothermic reaction increases with increasing temperature.

Q. 4. State whether the following statements are True or False. Justify your answers in brief.

- (i) Cu^+ disproportionates to Cu^{2+} and elemental copper in solution.
 (ii) Nitric oxide, through an odd electron molecule, is diamagnetic in liquid state
 (iii) The boiling point of propionic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight.



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Q. 9. The following questions consist of two statements, one labelled as **ASSERTION (A)** and the other labelled as **REASON (R)**. You are to examine these two statements carefully and decide if the **ASSERTION (A)** and the **REASON (S)** are individually true and if so, whether the Reason is a correct explanation of the Assertion. Select your answers to these items using the codes given below and mark your answer-sheet accordingly.

- (A) Both A and R are true, and R is the correct explanation of A.
 (B) Both A and R are true, and R is not the correct explanation of A.
 (C) A is true, but R is false.
 (D) A is false, but R is true.

| Assertion | Reason |
|--|---|
| 1. Between SiCl_4 and CCl_4 , only SiCl_4 reacts with water. | SiCl_4 is ionic and CCl_4 is covalent. |
| 2. In any ionic solid $[\text{MX}]$ with Schottky defects, the number of positive and negative ions are same. | Equal number of cation and anion vacancies are present. |
| 3. Addition of bromine to trans-2-butene yields meso-2, 3-dibromobutane. | Bromine addition to an alkene is an electrophilic addition. |
| 4. In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents. | The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. |
| 5. Dimethylsulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds. | It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. |

- Ans.**
- (C) : Si has vacant *d* orbital.
 - (A) : Schottky defect is defined as a vacancy developed for anion and cation site, so cation and anion vacancy will be same in number. Therefore, in an ionic solid MX with Schottky defects will still have the number of anions and cations same.
 - (B) : Bromine is *trans* addition,. Hence, *meso*.
 - (D) : When aniline is present in strongly acidic solution, it gets protonated and therefore becomes strongly deactivating for electrophilic substitution.
 - (A) : Ozonide can be reduced by $(\text{CH}_3)_2\text{S}$ to give carbonyl compounds and dimethyl sulphoxide.



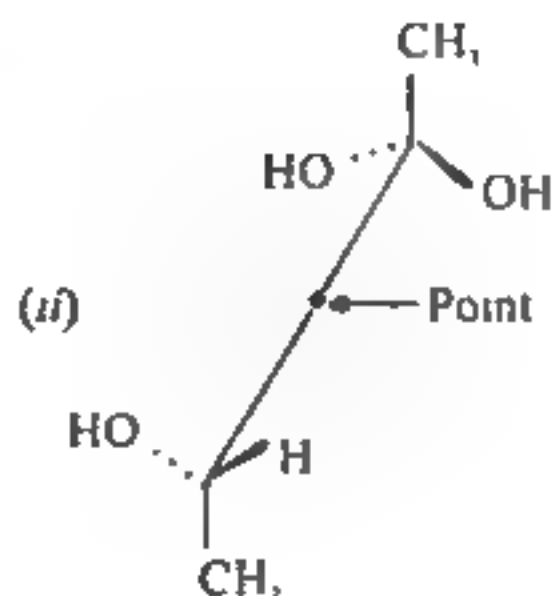
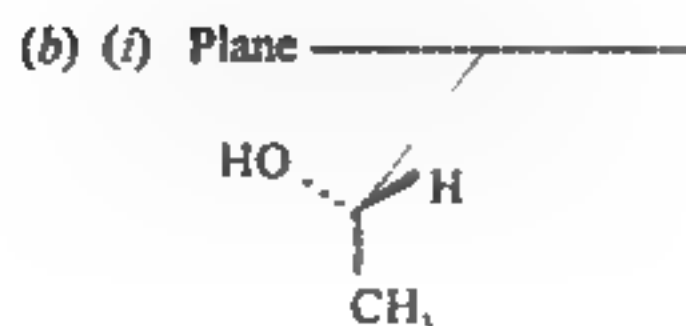
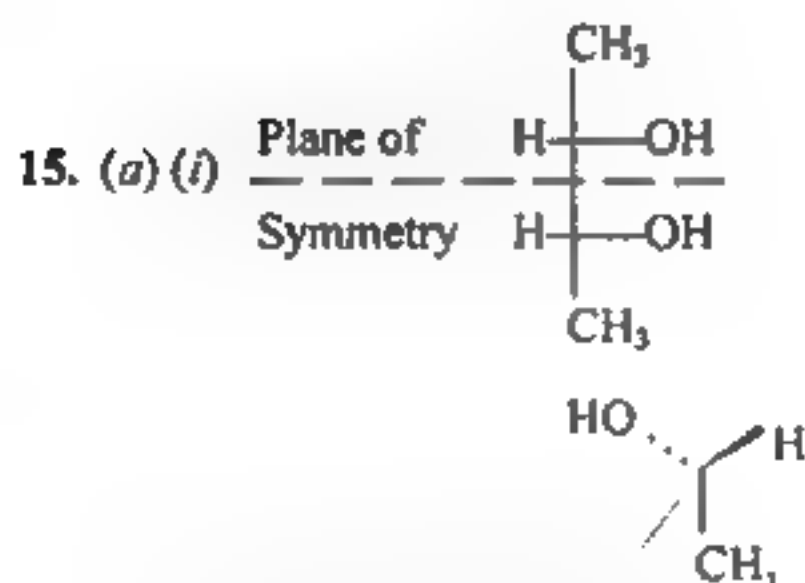
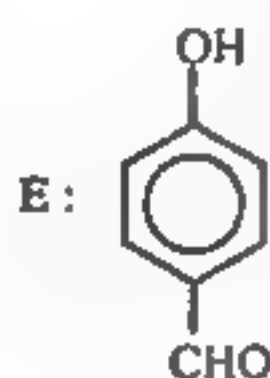
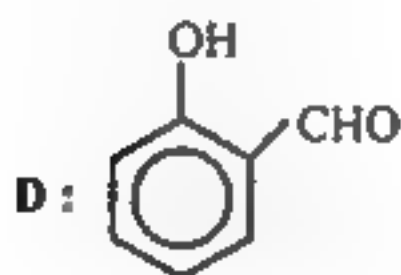
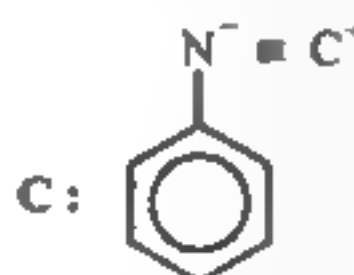
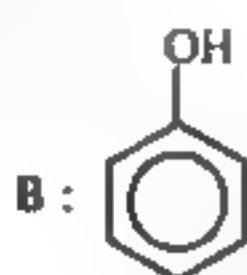
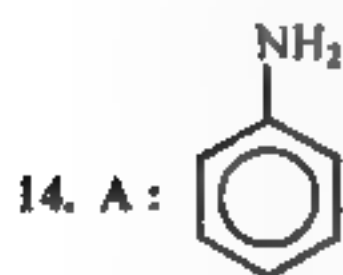
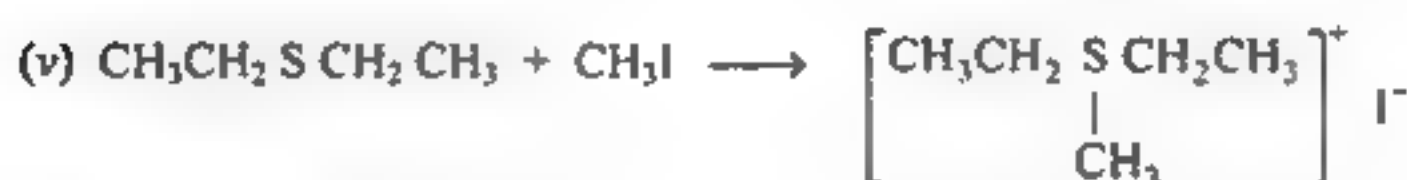
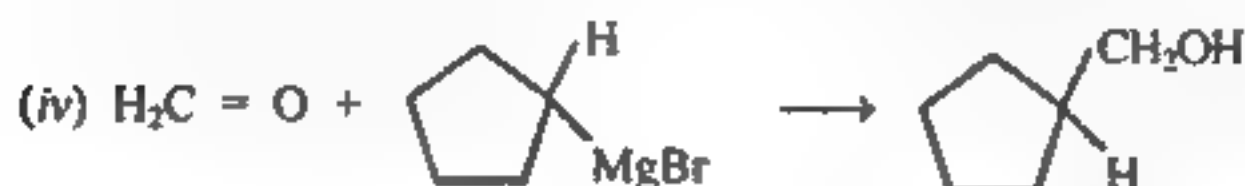
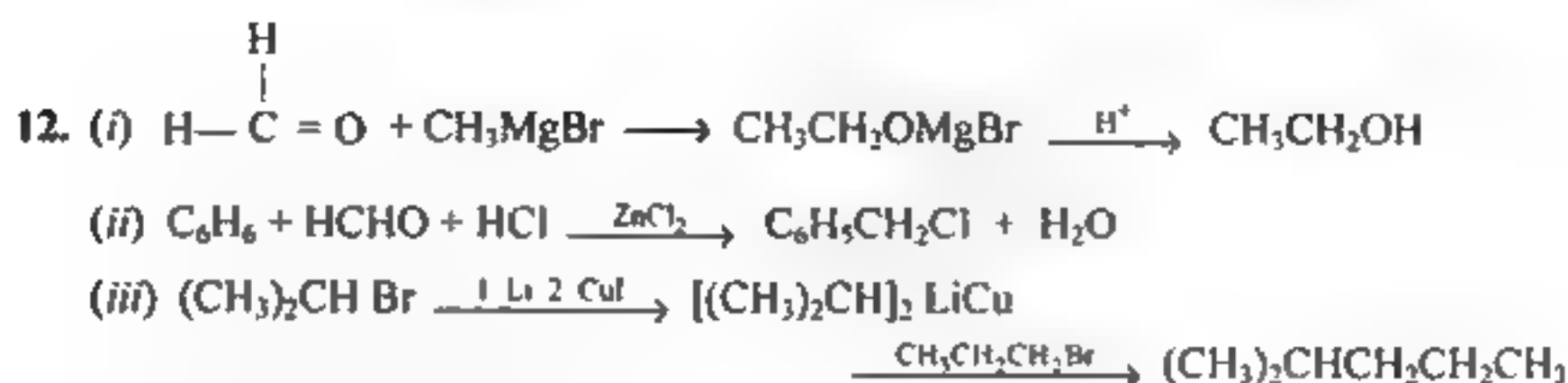
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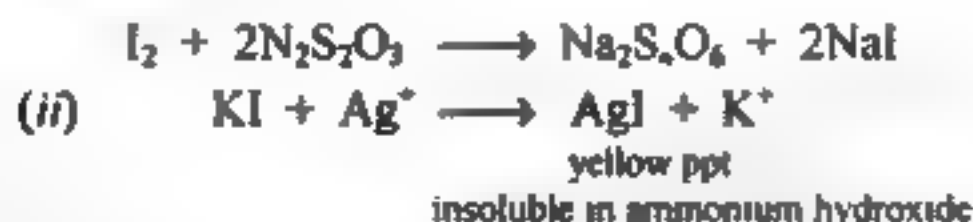
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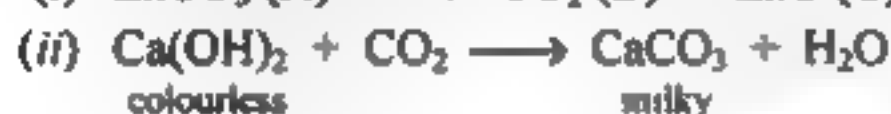


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15. Compound (A) is ZnCO_3 ; Compound (B) is CO_2 ;
Compound (C) is ZnO ; Compound (D) is ZnS

Since the gas (B) turn lime water milky, compound (A) is carbonate. Since solution of (A) gives white precipitate on passing H_2S in excess of NH_4OH , cation in (A) is Zn^{2+} . Therefore, compound (A) is zinc carbonate.



Practice Paper No.4

(IIT/JEE)

(CHEMISTRY MAINS)

Time : 2 Hours

Max. Marks : 100

Q. 1. An argon laser emits blue light with a wavelength of 488 nm. How many photons are emitted by this laser in two seconds if it operates at a power of 515 milliwatts? (5)

Q. 2. 50 mL of ozonized oxygen at STP were passed through KI solution to liberate iodine. The liberated iodine required 4.5 mL of N/10 sodium thiosulphate solution. What is the volume of ozone at STP in the ozonized oxygen. (5)



Q. 3. A bulb containing 4 litres of N_2 and 4 litres of CO_2 at STP is connected to a fully evacuated second bulb by a stop-cock with a small opening. The bulb is opened for 15 minutes and then closed. The first bulb is now found to contain 2 g of N_2 . Determine the percentage composition by weight of these gases in the second bulb. (5)

Q. 4. Carborundum (SiC) is prepared industrially by the following reaction : (5)



ΔH° for this reaction is 624.6 kJ and the ΔH°_f for $\text{SiO}_2(\text{s})$ and $\text{CO}(\text{g})$ are -910.9 kJ/mol and -110.5 kJ/mol respectively. Calculate standard heat of formation of silicon carbide.

Q. 5. Given that : (5)





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SOLUTIONS

1. 28 photons

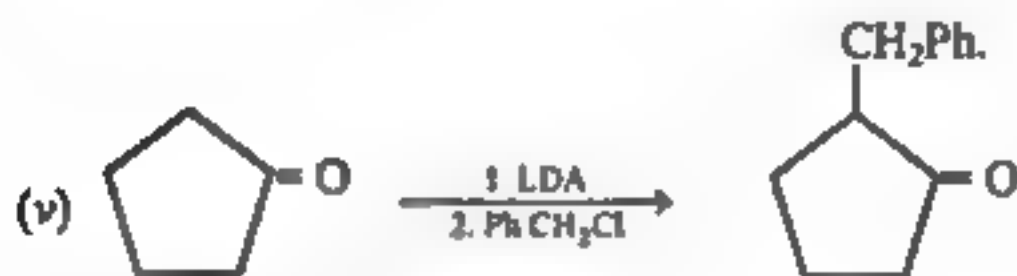
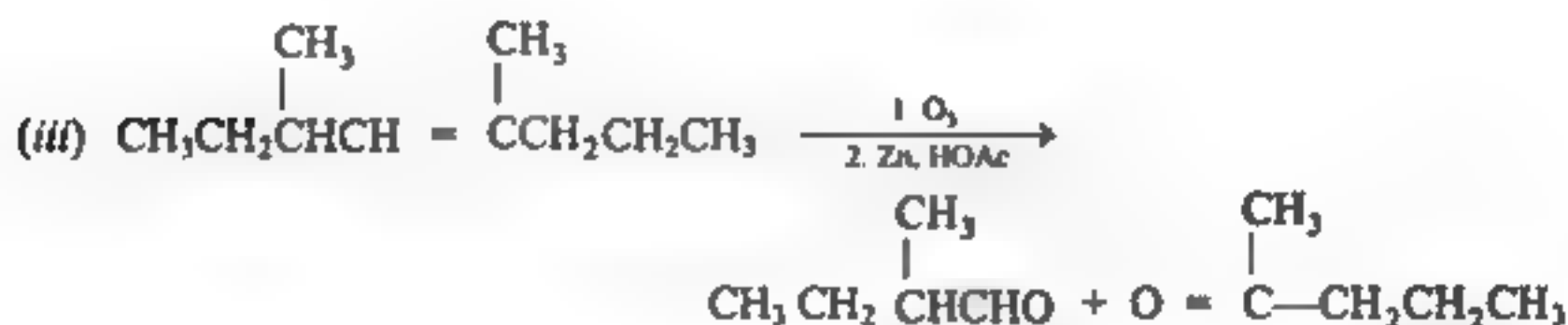
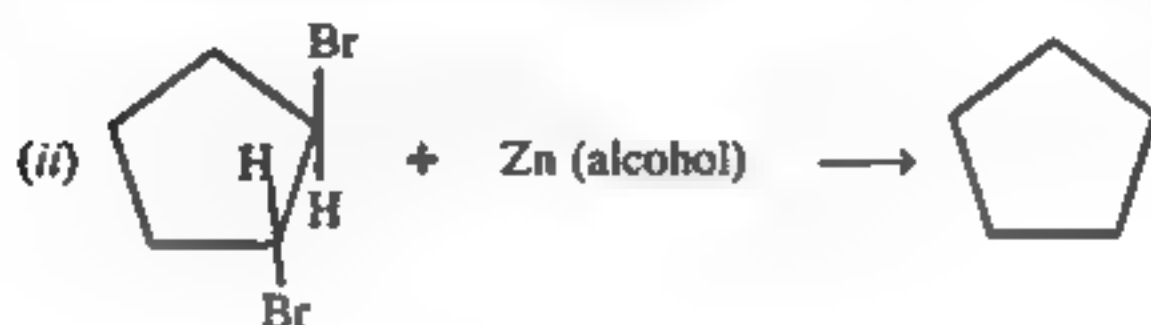
3. 1.7 g/L

5. $6.0 \times 10^{-5} \text{ atm}^{-1}$

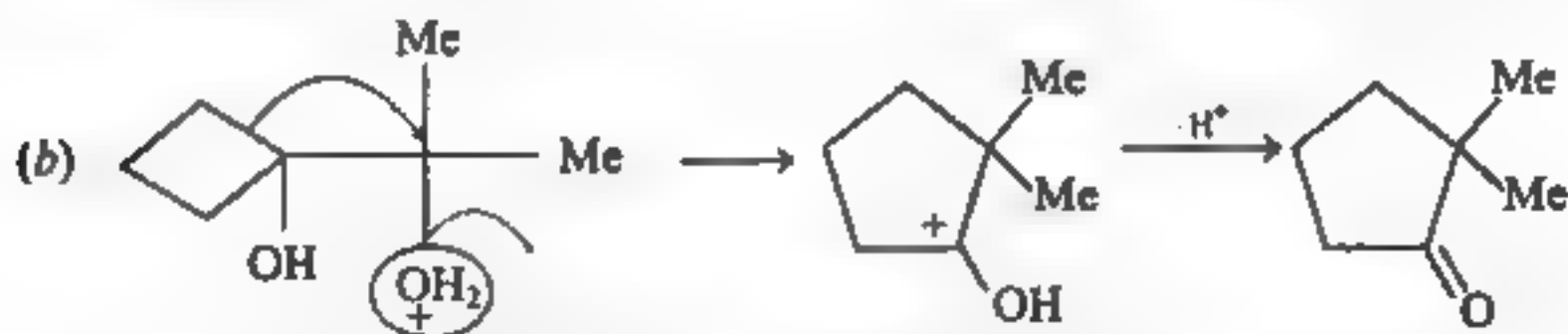
7. 0.456 g

2. $\text{NaCl} = 28.3\%$ 4. $-509.5 \text{ kJ}, -43.5 \text{ kJ/mol}$

6. 8.94

8. First order, 25600 bacteria
 $k = 0.046 \text{ min}^{-1}$ 9. (i) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{alc. KOH} \longrightarrow \text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ 

10. 4-methyl-2-pentyne

11. A : CH_3OH B: CH_3COCH_3 C : HCHO D : HCOOH 12. (a) RS^- is a better nucleophile than RO^- because RS^- is a much weaker base than RO^- . Therefore, elimination with RS^- is not as serious a problem as with RO^- .

This is a pinacol-pinacolone rearrangement in which the side of a ring is the migrating group. This leads to ring expansion. Formation of the cyclobutyl C^+ is unlikely because the ring strain increases in going from 90°C to 120° .

(c) $\text{A} > \text{B} > \text{C}$. (A) is the most acidic because the $-ve$ charge is delocalized on two oxygen atoms which results in the additional stabilization of the conjugate base.



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But the unit g/cm³ for density is widely used. The commonly used unit for gases is g/litre.

1 g/ml = 1 kg/litre
= 1000 kg/m³ = 1000 g/litre
1 g/litre = 1 kg/m³

8. **Concentration.** It is defined as the amount of a solute per unit volume of solution. The derived SI unit of concentration is mol m⁻³.

Concentration = $\frac{\text{Mass of the solute}}{\text{Volume of solution}}$ = $\frac{\text{mol}}{\text{m}^3}$ = mol m⁻³

But the commonly used unit is mol/dm³ also written as mol/litre. A solution with a concentration of 1 mol/dm³ is said to be 1 molar (1 M). Other units in use are molality, normality, mole-fraction and mol percent.

Derived SI Units

| Physical quantity | Symbol | SI Unit | Symbol | Definition |
|-------------------------------|--------|--------------------------|--------|--|
| Area | A | square metre | | m ² |
| Volume | V | cubic metre | | m ³ |
| Density | ρ | kilogram per cubic metre | | kg m ⁻³ |
| Velocity | v | metre per second | | ms ⁻¹ |
| Acceleration | a | metre per sec per sec | | ms ⁻² |
| Concentration | — | mol per cubic metre | | mol m ⁻³ |
| Energy | E | Joule | J | kg m ² s ⁻² |
| Force | F | Newton | N | kg ms ⁻² or Jm ⁻¹ |
| Power | — | Watt | W | kg m ² s ⁻³ Js ⁻¹ |
| Pressure | P | Pascal | Pa | kg m ⁻¹ s ⁻² Nm ⁻² |
| Frequency | ν | Hertz | Hz | cycles per second |
| Electric charge | Q | Coulomb | C | As |
| Electric potential difference | V | volt | V | kg m ² s ⁻³ A ⁻¹ or J A ⁻¹ s ⁻¹ kg m ² s ⁻³ A ⁻² or V A ⁻¹ |
| Electric resistance | R | ohm | Ω | m ² kg ⁻¹ S ³ A ² Ω ⁻¹ |
| Electric conductance | G | Siemens | S | |
| Electric capacitance | — | Farad | F | A ² s ⁴ kg ⁻¹ m ⁻² or As V ⁻¹ |
| Magnetic flux | Φ | Weber | Wb | kg m ² s ⁻² A ⁻¹ |
| Magnetic flux density | B | Tesla | T | kg s ⁻² A ⁻¹ |

APPENDIX – G

Units allowed in Conjunction with SI Units

| Quantity | Name | Symbol | Definition |
|----------|---------|--------|---|
| Length | Parsec | pc | 30.87 × 10 ¹⁵ m |
| Area | Barn | b | 10 ⁻²⁸ m ² |
| | Hectare | ha | 10 ⁴ m ² |
| Volume | Litre | L | 10 ⁻³ m ³ = dm ³ |



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Report 10.850 as 10.8 if there are three significant figures.

Report 93.450 as 93.4 if there are three significant figures.

- (c) In case of multiplication, the value should be reported to the same number of significant terms as is possessed by the least precise term. The number 159.3 has four significant figures and the number 0.17 has two significant figures and so the result should be reported to two significant figures.

$$159.3 \times 0.17 = 27.081$$

Report it as 27.

- (d) In case of division, round off the numbers to numbers with one more significant figure than required in the result, before division is carried out

$$9.0583 \left(\frac{7.3321}{24} \right) = 9.6 \left(\frac{7.33}{24} \right) = 2.767$$

Report it as 2.8.

- (e) The length 8 cm can also be represented as 0.08 m since 1 cm = 0.01 m. In this case, the zero has been put to locate the decimal point and is not a significant figure. Zero in a number is a significant number only when it is found to be zero by measurement.

For a given quantity measured as 0.006090, the zeroes after 6 are only significant.

The zeroes pose serious difficulties in knowing the number of significant figures in a number. The numbers 489 and 489.0 do not have the same significant figures. In 489, 9 is the doubtful figure whereas in 489.0, 0 is the doubtful figure. These difficulties are removed by using scientific notation in which the number is expressed as powers of 10 and the coefficient between 1 and 10. The exponential part gives only the magnitude of the quantity and has nothing to do with the significant figures.

4.800×10^3 means 4800 ± 1 Four significant figures

4.80×10^3 means 4800 ± 10 Three significant figures

4.8×10^3 means 4800 ± 100 Two significant figures

4×10^3 means 4000 ± 1000 One significant figure

APPENDIX – N

Units in Chemical Calculations

The numbers in chemical calculations should always carry units and undergo the same mathematical operations as the numbers. Some units may cancel out and the remaining units should always be reported as a part of the answer. Most of the problems may be solved by the unity-method or use of conversion factors.

Example 1. Calculate the moles of oxygen in 48 g oxygen gas.

Molecular mass $O_2 = 32$ g/mol

$$\text{Moles } O_2 = \frac{\text{Mass } O_2}{\text{Molecular mass } O_2} = \frac{48 \text{ g}}{32 \text{ g/mol}} = 1.5 \text{ mol } O_2$$

Example 2. 0.9375 g of an organic compound contains 0.1326 g of chlorine. What is mass percent chlorine in the sample?



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$$67. \quad \text{Specific heat} = \frac{\text{Heat capacity of a substance}}{\text{Heat capacity of water}}$$

$$68. \quad \text{Specific heat} \times \text{Atomic mass} \approx 6.3$$

$$69. \quad c = \frac{q}{n \Delta T}$$

$$70. \quad C_p - C_v = R$$

$$C_p = \frac{5}{2} R$$

$$71. \quad H = E + PV$$

$$\Delta H = \Delta E + P \Delta V$$

$$\Delta H = \Delta E + \Delta n RT$$

$$72. \quad \Delta E = q + w$$

$$73. \quad W_{\text{rev}} = -nRT \, 2.303 \log V_2/V_1$$

$$74. \quad W_{\text{rev}} = -nRT \, 2.303 \log P_1/P_2$$

$$75. \quad W_{\text{ir}} = -P_{\text{ext}}(V_2 - V_1)$$

$$76. \quad W_{\text{rev (adia)}} = nC_v(T_2 - T_1)$$

$$77. \quad \left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$78. \quad \Delta H^{\circ}_{\text{reaction}} = \Sigma H^{\circ}_{f, \text{products}} - \Sigma H^{\circ}_{f, \text{reactants}}$$

$$79. \quad \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots \dots$$

$$80. \quad \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

$$81. \quad \Delta H_{\text{solution}} = \Delta H_{\text{hydration}} - \Delta \text{Lattice energy}$$

$$82. \quad \text{Enthalpy change in a reactants} = \frac{\text{Sum of bond energies}}{\text{of reactants}} - \frac{\text{Sum of bond energies}}{\text{of products}}$$

$$83. \quad \Delta S_{\text{total}} = \frac{+q}{T_{\text{system}}} + \frac{-q}{T_{\text{surroundings}}}$$

$$84. \quad \Delta S^{\circ} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}}$$

$$85. \quad G = H - TS$$

$$\Delta G = \Delta H - T \Delta S$$

$$86. \quad \Delta G^{\circ} = \Sigma \Delta G^{\circ}_{f, \text{products}} - \Sigma \Delta G^{\circ}_{f, \text{reactants}}$$

$$87. \quad \Delta G^{\circ} = -RT \ln K$$

$$\log K = -0.175 \Delta G^{\circ} \text{ kJ mol}^{-1} \text{ at } 25^{\circ}\text{C}$$

$$88. \quad \Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

$$\Delta S = 2.303 nR \log \frac{P_1}{P_2}$$

$$89. \quad \Delta G = 2.303 nRT \log \frac{V_1}{V_2}$$



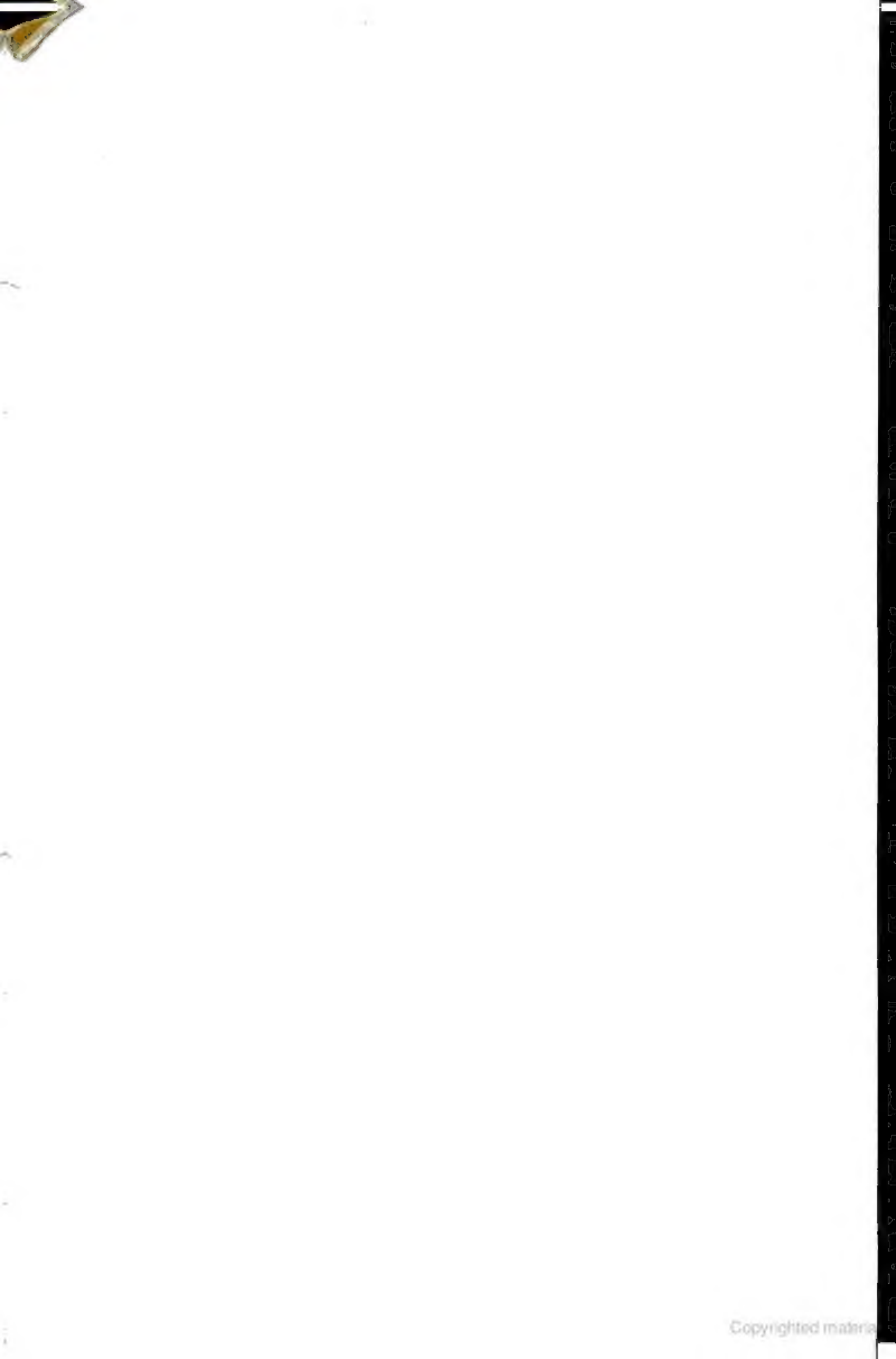
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